

AD-A091 631

NATIONAL BUREAU OF STANDARDS WASHINGTON DC CHEMICAL --ETC F/G 4/1
CHEMICAL KINETIC AND PHOTOCHEMICAL DATA SHEETS FOR ATMOSPHERIC --ETC
APR 80 R F HAMPSON DOT-FA79WAI-005

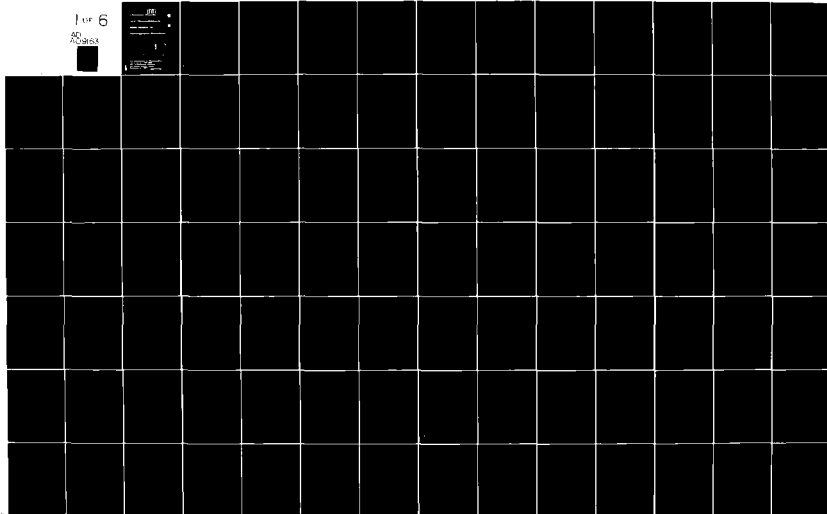
UNCLASSIFIED

FAA/EE-80-17

NL

1 of 6

AD-A091 631



LEVEL II

①

Chemical Kinetic

and Photochemical

Data Sheets for

Atmospheric Reactions

R.F. Hampson

Chemical Kinetics Division
Center for Thermodynamics
and Molecular Science
National Bureau of Standards

DTIC
ELECTE

NOV 07 1980

E

80 11 04 058

AD A091631

Technical Report Documentation Page

| | | | |
|--|--|--|--|
| 1. Report No. FAA/EE-80-17 | 2. Government Accession No. AD-A091631 | 3. Recipient's Catalog No. | |
| 4. Title and Subtitle CHEMICAL KINETIC AND PHOTOCHEMICAL DATA SHEETS FOR ATMOSPHERIC REACTIONS | | 5. Report Date Apr 1980 | 6. Performing Organization Code |
| 7. Author(s) R. F. Hampson | | 8. Performing Organization Report No. | |
| 9. Performing Organization Name and Address Chemical Kinetics Division Center for Thermodynamics and Molecular Science National Bureau of Standards Washington, D.C. | | 10. Work Unit No. (TRAIS) | 11. Contract or Grant No. DOT-FA79WAI-005 |
| 12. Sponsoring Agency Name and Address U.S. Department of Transportation Federal Aviation Administration High Altitude Pollution Program Washington, D.C. 20591 | | 13. Type of Report and Period Covered | 14. Sponsoring Agency Code |
| 15. Supplementary Notes Also sponsored by: National Aeronautics and Space Administration National Bureau of Standards Upper Atmosphere Research Office Office of Standard Reference Data Washington, D.C. Washington, D.C. | | | |
| 16. Abstract A set of individual data sheets for gas phase chemical reactions and photochemistry of neutral species is presented. These data sheets give preferred values for reaction rate constants, photoabsorption cross sections and quantum yields with a brief statement discussing the basis for the preferred value. Recent experimental results are also given. The coverage of this initial set of data sheets issued in February 1980 corresponds to the approximately 400 reactions listed in NBS Special Publication 513, R. F. Hampson and D. Garvin, May 1978. For approximately one quarter of these reactions the data entry has been updated to include the 1979 recommendations of the NASA Panel for Data Evaluation and the CODATA Task Group on Chemical Kinetics. They are intended to provide the basic physical chemical data needed as input data for calculations modeling atmospheric chemistry. Revisions and additions for specific reactions will be published as new information becomes available. | | | |
| 17. Key Words Air pollution; atmospheric chemistry; chemical kinetics; data evaluation; gas phase; photoabsorption cross section; photochemistry; quantum yield; rate constant. | | 18. Distribution Statement Available through the National Technical Information Service, Springfield, Virginia 22161. | |
| 19. Security Classif. (of this report) UNCLASSIFIED | 20. Security Classif. (of this page) UNCLASSIFIED | 21. No. of Pages 490 | 22. Price |

4 3402+

21

1. Introduction

A set of individual data sheets on the chemical kinetics and photochemistry of neutral species is presented. They are designed for use in modeling the chemistry of the stratosphere and, to a more limited extent, the polluted troposphere and also the interpretation of laboratory experiments.

The coverage of this initial set of data sheets issued in February 1980 corresponds to the approximately 400 reactions listed in NBS Special Publication 513, "Reaction Rate and Photochemical Data for Atmospheric Chemistry - 1977", R. F. Hampson and D. Garvin, May 1978. Approximately one quarter of these reactions were among those considered by the NASA Panel for Data Evaluation in June 1979 at the Stratosphere Workshop in Harpers Ferry, West Virginia. The Panel recommendations are given in NASA Reference Publication 1049, "The Stratosphere: Present and Future", R. D. Hudson and E. I. Reed editors, December 1979. For these reactions the data entry has been updated to include the NASA 1979 recommendation and explanatory note. The date of preparation of these data sheets is shown as June 1979. For the remaining reactions the data entry itself has not been updated from that given in NBS Special Publication 513 and therefore the date shown on these data sheets is May 1978, the publication date for NBS SP 513.

The Chemical Kinetics Data Center has issued four versions of a table of rate data in the following National Bureau of Standards publications: NBSIR 73-203 (1973); NBSIR 74-430 (1974); NBS Technical Note 866 (1975); and NBS Special Publication 513 (1978). The present data sheets supersede all these earlier publications.

| | |
|--------------------|--|
| For | |
| AI | <input checked="checked" type="checkbox"/> |
| ed | <input type="checkbox"/> |
| ion | <input type="checkbox"/> |
| Distribution/ | |
| Availability Codes | |
| Dist. | Avail and/or special |
| A | |

Rate data evaluation is a small but growing branch of physical chemistry. Evaluations and compilations of rate data and on-going programs in these areas have been described in the review paper "Evaluation and Compilation of Reaction Rate Data" by R. F. Hampson and D. Garvin, Journal of Physical Chemistry **81**, 2317-2319 (1977). An extensive listing of sources of evaluated rate data, NBS List of Publications 73 "Chemical Kinetics Tables, Data Evaluations and Bibliographies. A Guide to the Literature" is available on request from the NBS Chemical Kinetics Data Center.

In addition to the data evaluation activities at the National Bureau of Standards, these are major ongoing rate data evaluation efforts by two panels of which the present author is a member. One is the NASA Panel for Data Evaluation which as mentioned previously has published its 1979 recommendations in NASA Reference Publication 1049, December 1979. The other is the CODATA Task Group on Chemical Kinetics whose recommendations will be published in 1980 in the Journal of Physical and Chemical Reference Data. Recommendations of both panels are included in these data sheets where appropriate. The only significant difference in recommendations by these panels is for the reactions of $O(^1D)$ atoms. In these cases the present author has chosen to accept the recommendations of the NASA panel.

In addition to recommendations on rate and photochemical data the data sheets include listings of current research results. These data listings serve several purposes. Some simply record measurements, usually limited in number, on reactions for which it is not yet practical to give recommended values. Others show the data upon which a new recommendation is based. Still others show what has been done on a

reaction since its rate constant was last evaluated. These new data may support the recommendation or suggest the need for modifications in the future.

2. Guide to the Data Sheets

2.1 General

These data sheets provide current information on reaction rate constants, quantum yields and absorption cross sections. For many reactions, preferred values are given. The reactions included in this initial set of data sheets are summarized in the index of reactions given in section 3.

Each data sheet contains the following items:

- a. A statement of the chemical reaction.
- b. The value of the enthalpy of the reaction calculated from the table of thermochemical data in the forthcoming report of the CODATA Task Group on Chemical Kinetics.
- c. The data entry for each reaction as given in NBS Special Publication 513 but revised to include the 1979 recommendations of the NASA Panel for Data Evaluation and the CODATA Task Group on Chemical Kinetics where pertinent.
- d. Where a recommended value is given, there is a brief statement discussing the basis for the recommendation. In those instances where the recommendation is that of the NASA Panel for Data Evaluation, the statement given in the note of the NASA panel for that reaction as given or cited in NASA Reference Publication 1049.
- e. A list of references.
- f. The date of the recommendation or the date through which the literature coverage extends. As indicated earlier the date shown is either May 1978 or June 1979.

Recommended values are usually indicated by an asterisk placed ahead of the entry in the reference column. However in those instances where the first entry is either "NASA (1979) eval" or "CODATA (1979) eval" the asterisk has been omitted and it is simply implied that this entry is the recommended value.

2.2 Uncertainty in Recommended Value of a Rate Constant

The uncertainty assigned here to the recommended value of a rate constant is given in the column "Uncert. Factor at 298 K, notes". This is an estimate by the evaluator of the absolute accuracy of the preferred value. It is a subjective judgment derived from intercomparison of data sets, consideration of related reactions studied with the same technique, estimates of how well the parameters could have been controlled, and comparison with theory. It means that in the evaluators judgment, the true value will lie within the indicated limits to a high level of confidence.

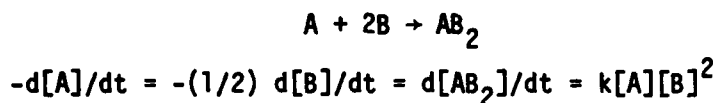
The uncertainty factor is given for the value of the rate constant at 298 K. The statement that the rate constant k has the central value k_0 and is uncertain to a factor f means that the true value of k lies in the range between k_0/f and $k_0 f$. An estimate of the uncertainty factor for temperatures below 298 K is given by the following expression:

$$f_T/f_{298} = \exp[(1/T - 1/298)\Delta(E/R)]$$

At times a rate constant expression is quoted with individual uncertainties for the rate parameters as $k = (A \pm a) \exp(-B \pm b/T)$. These measures are those provided by the author of the paper and often are indications of precision, not overall reliability.

2.3 Conventions Concerning Rate Constants

a. General Convention. Almost all of the reactions listed here are elementary processes. For them the rate expression is derivable from a statement of the reaction, e.g.



Note that the stoichiometric coefficient for B, i.e. 2, appears in the denominator before B's rate of change (which is equal to $2k[A][B]^2$) and as a power on the right hand side.

b. Combination Reactions. Some reactions of this type are not of integral kinetic order over the stratospheric pressure and temperature range. That is, although they require an energy transfer agent, "M", they are in the "pressure fall-off region". For some such reactions we tabulate the low pressure limiting third order rate constant k_0 in units of $\text{cm}^6 \text{molecule}^{-2} \text{s}^{-1}$ and the high pressure limiting second order rate constant k_∞ in units of $\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$. The expression for the value of the rate constant in the pressure fall-off range is given by the expression developed by J. Troe in J. Phys. Chem. 83, 114 (1979):

$$\log k = \log[k_0[M]/(1 + k_0[M]/k_\infty)] + \log F_c/(1 + [\log k_0[M]/k_\infty]^2)$$

For the recommendations of the CODATA panel the value of F_c is 0.8; the recommendations of the NASA panel are based on the value of 0.6 for F_c .

c. Forward and Reverse Reactions. In some cases there are no data on a reaction of interest but there are data on the reverse reaction. Occasionally, an evaluation will use the data on the reverse reaction together with the equilibrium constant to calculate the rate constant.

Obviously this is an approximation but it often is a useful method of estimating non-measured physical properties. The entry contains notations to tell the reader when this procedure has been used, such as "based on reverse reaction", or when both reactions f and r are listed together " $k_f = k_r K_{eq}$ " or $k_r = k_f / K_{eq}$. These expressions, which are those used in the analyses, are based on equating the two rates at equilibrium.

2.4 Convention Concerning Optical Absorption Coefficients

These are reported as "absorption cross sections per molecule, base e". They are defined by the equation:

$$\sigma = (1/([N]\ell)) \ln (I_0/I)$$

where I_0 and I are the intensities of incident and transmitted light, σ is the absorption cross section, $\text{cm}^2 \text{molecule}^{-1}$, $[N]$ is the concentration of absorbers, molecules cm^{-3} , and ℓ is the path length, cm. Other definitions and units are frequently used. The terms "absorption coefficient" and "extinction coefficient" are common. It is always necessary to know what concentration units, path length units and type of logarithm (base e or base 10) are used in the definition. To convert "cross-sections" to absorption coefficients in $(\text{atm at } 273 \text{ K})^{-1} \text{ cm}^{-1}$, base e, multiply by 2.69×10^{19} .

3. Ordering of the Data Sheets

Data on a reaction appear only once in these data sheets. The normal location for a reaction is determined by its reactants. Each species has been assigned a sequence number (1 to 65) as shown in the index that follows. These sequence numbers are the same as those used in NBS Special Publication 513. The ordering of reactions is the same as in NBS SP 513 but with two exceptions - more pairs of forward and reverse reactions

have been combined into one entry, and all the photochemical data sheets have been consolidated and placed after the data sheets for chemical reactions. A reaction is filed under the lower numbered species. That is, the reaction of ozone (7) with an oxygen atom (1) is filed under reactions of oxygen atoms. The numbers for the reactants appear at the left margin of the table, preceding the statement of the reaction, e.g. 1,7 O + O₃ → O₂ + O₂. These number pairs run in ascending order through the table. If a reaction is not found in the location described above, the reader should look for it under the reverse reaction. The usual rule is that exothermic reactions are given as the "forward" reactions.

In the index that follows, bimolecular reactions are listed under both reactants. Frequently the listing of reaction partners for a particular species is divided into two parts by three dashes, separating species earlier in the list than the species indexed from those later in the list. Reactions of the particular species with those species listed before the three dashes should be sought under those reaction partners. There is no indexing of products of reactions. A few species are listed in the index for which there are no reactions in the table, in anticipation of expansion of the data set.

ACKNOWLEDGMENT

This work was supported, in part, by the High Altitude Pollution Program of the Office of Environment and Energy, Federal Aviation Administration and the Upper Atmosphere Research Office of the National Aeronautics and Space Administration. It was also supported, in part by the Office of Standard Reference Data, National Bureau of Standards.

| | | |
|-------------------------------------|--|--|
| 1. O | Reacts with: O, O(¹ S), O ₂ , O ₃ , N, NO, NO ₂ , NO ₃ , N ₂ , N ₂ O, N ₂ O ₄ , N ₂ O ₅ , NH ₃ , H, HO, HO ₂ , H ₂ , H ₂ O, H ₂ O ₂ , HNO ₂ , HNO ₃ , HNO ₄ , SO, SO ₂ , SO ₃ , HS, H ₂ S, CS, CS ₂ , COS, ClO, BrO, FO, SOClO, FO ₂ , HCl, HBr, HClO, NO ₂ Cl, Cl ₂ , Cl ₂ O, CO, CO ₂ , CN, CNO, CH ₂ O, CH ₃ , CH ₃ NO ₂ , CH ₃ NO, CH ₄ , C ₂ H ₄ , C ₂ H ₆ , C ₃ H ₈ , alkane, C ₆ H ₆ , C ₆ H ₅ CH ₃ , CH ₃ Cl | |
| 2. O(¹ D) | Reacts with: O ₂ , O ₃ , NO, NO ₂ , N ₂ , N ₂ O, NH ₃ , H ₂ , H ₂ O, H ₂ O ₂ , HCl, HF, CO ₂ , CH ₄ , C ₂ H ₆ , CF ₂ Cl ₂ , CFCI ₃ , CF ₂ O, CFCI ₂ O, CCl ₂ O | |
| 3. O(¹ S) | Reacts with: O, O ₂ , O ₃ , NO, NO ₂ , N ₂ , N ₂ O, NH ₃ , H ₂ O, CO ₂ , CH ₄ | |
| 4. O ₂ | Reacts with: O, O(¹ D), O(¹ S) - - - N, NO, NO ₂ , NO ₃ , N ₂ , H, H ₂ , H ₂ O, H ₂ O ₂ , HNO, SO, HS, Cl, F, CN, CH ₄ , CH ₃ , CH ₃ O | |
| 5. O ₂ (¹ Δ) | Reacts with: O ₂ , O ₃ , N, NO, N ₂ , H, SO, SO ₂ , H ₂ S, CO, CF ₂ Cl ₂ , CCl ₄ , CH ₃ Cl, CH ₂ Cl ₂ , CHCl ₃ | |
| 6. O ₂ (¹ Σ) | Reacts with: O ₂ , N ₂ , H ₂ O | |
| 7. O ₃ | Reacts with: O, O(¹ D), O(¹ S), O ₂ (¹ Δ) - - - N, N, NO, NO ₂ , H, HO, HO ₂ , HNO ₂ , SO, SO ₂ , H ₂ S, Cl, Br, F, ClO, BrO, FO, CO, CH ₂ O, CH ₃ , CH ₃ O ₂ , CH ₃ NO, CH ₄ , C ₂ H ₄ , C ₃ H ₆ , allene, butenes, butadiene, C ₂ Cl ₂ H ₂ | |

8. N
Exn with: O, O₂, O₂(¹A), O₃ - - -
N, NO, NO₂, NO, SO, SO₂, SO₃, SO₄
9. NO
Exn with: O, O(¹D), O(¹S), O₂, O₂(¹A), O₃, N - - -
M, NC, NO₂ + H₂O, NO₃, NH₃, NH₄, H, HC,
H₂O, H₂, H₂O, H₂O₂, Cl, F, ClO, BrO, FO,
OClO, CH₃, CH₃O, CH₃O₂
10. NO₂
Exn with: O, O(¹D), O(¹S), O₂, O₃, N, NO + H₂O - - -
M, NC, NO₃, NH₃, H, FO, NO₂, SO₂,
Cl, F, ClO, BrO, FO, CH₃, CH₃O, CH₃O₂
11. NO₃
Exn with: O, O₂, NO, NO₂ - - -
M, NO₃, H₂O, SO₂
12. N₂
Exn with: O, O(¹D), O(¹S), O₂, O₂(¹A), O₂(¹Σ) - - -
M, NC
13. N₂O
Exn with: O, O(¹D), O(¹S) - - -
M, H, NO, ClO, CO
14. N₂O₅
Exn with: O - - - M, H₂O, SO₂
15. NH
Exn with: NO - - -
16. NH₂
Exn with: O, NO - - - H, NO, H₂, H₂O
17. NH₃
Exn with: O, O(¹D), O(¹S), NO₂ - - -
M, H, NO, ClO

| | | |
|------------------------------------|--|--|
| 17a. N ₂ H ₄ | Exn with: H | |
| 18. H | Exn with: O, C ₂ , O ₂ (¹ Δ), O ₃ , NO, NO ₂ , N ₂ O, NH ₂ , NH ₃ , N ₂ H ₄ - - - | |
| | H, H ₂ , H ₂ O, H ₂ O ₂ , H ₂ O, H ₂ O ₂ , HNO, HNO ₂ , HNO ₃ , SO ₂ , HS, H ₂ S, COS, OCl ₂ , HCl, NOCl, Cl ₂ , CO, CO ₂ , CH ₂ O, CH ₃ OH, CH ₃ CHO, CH ₃ Cl | |
| 19. H ₂ | Exn with: O, O ₃ , N, NO, NO ₂ , N ₂ , N ₂ O, NH ₂ , NH ₃ , H - - - | |
| | M, H ₂ , H ₂ O ₂ , H ₂ , D ₂ , H ₂ O, H ₂ O ₂ , HNO, HNO ₂ , HNO ₃ , HNO ₃ , HNO ₄ , SO ₂ , H ₂ S, CS ₂ , COS, Cl, Cl ₂ , Br ₂ , HCl, DCl, HBr, H ₂ Cl, NO ₃ Cl, CO, CH ₂ O, CH ₃ OH, CH ₃ CHO, CH ₃ NO ₂ , CH ₃ ONO, CH ₄ , C ₂ H ₂ , C ₂ H ₄ , C ₂ H ₆ , C ₃ H ₆ , C ₄ H ₁₀ , alkane, C ₆ H ₆ , C ₆ H ₅ CH ₃ , CF ₂ Cl ₂ , CFCl ₃ , CCl ₄ , CH ₃ Cl, CH ₂ Cl ₂ , CHCl ₃ , C ₂ Cl ₂ F ₂ | |
| 20. H ₂ O ₂ | Exn with: O, O ₃ , NO, NO ₂ , H, H ₂ - - - | |
| | M, H ₂ O ₂ , H ₂ , H ₂ O, SO ₂ , Cl, Br, Cl ₂ , Br ₂ , CO, CH ₂ O, CH ₃ O ₂ , C ₂ H ₄ , C ₂ H ₆ , C ₃ H ₈ , C ₄ H ₁₀ | |
| 21. H ₂ | Exn with: O, O(¹ D), O ₂ , NO, NH ₂ , H ₂ , H ₂ O - - - | |
| | M, Cl, F, Cl ₂ | |
| 22. H ₂ O | Exn with: O, O(¹ D), O(¹ S), O ₂ , O ₂ (¹ Σ), NO, NO ₃ , N ₂ O ₅ , NH ₂ , H, H ₂ O, H ₂ O ₂ - - - SO ₂ , F | |
| 23. H ₂ O ₂ | Exn with: O, O(¹ D), O ₂ , NO, H, H ₂ - - - | |
| | M, Cl, Br | |

| | |
|-------------------------------------|---|
| 24c. HNO | Run with: O ₂ , H, HO - - - M, HNO |
| 25c. HNO ₂ | Run with: O, C ₂ , H, HO - - - |
| 26c. HNO ₃ | Run with: O, H, HO - - - M, Cl |
| 26ac. HNO ₄ | Run with: C, Hc - - - |
| 26bc. S | Run with: CS ₂ , Cds |
| 27c. SO | Run with: O, C ₂ , O ₂ (¹ Δ), O ₃ , N - - - SO, SO ₂ |
| 28c. SO ₂ | Run with: O, O ₂ (¹ Δ), O ₃ , NO ₂ , NO ₃ , N ₂ O ₅ , H, HO, HO ₂ - - - CH ₃ |
| 29c. SO ₃ | Run with: O, N, H ₂ O, SO - - - |
| 30c. S ₂ O | Run with: |
| 31c. HS | Run with: O, O ₂ , H - - - HS |
| 32c. H ₂ S | Run with: O, O ₂ (¹ Δ), O ₃ , H, HO - - - |
| 33c. HSO ₂ | Run with: |
| 34c. H ₂ SO ₄ | Run with: |
| 34ac. CS | Run with: O - - - |
| 34bc. CS ₂ | Run with: O, Hc, S - - - |
| 34cc. COS | Run with: O, H, HO, S - - - |

35. Cl Exn with: $O_2, O_3, NO, NO_2, NO, NO_2, N_2, N_2O_2, NH_3, Cl, ClO, ClO_2, NOCl, NO_2Cl, NO_3Cl, Cl_2O, CH_2O, CH_4, C_2H_6, CH_3Cl$

35Br, Br Exn with: $O_3, NO_2, N_2O_2, - - -$

36F, F Exn with: $O_2, O_3, NO, NO_2, N_2, N_2O, - - - CH_4$

36. ClO Exn with: $O, O_2, NO, NO_2, N_2O, NH_3, NO, NO_2, N_2, - - - ClO, BrO, CO, CH_4, C_2H_2, C_2H_4$

36Br, BrO Exn with: $O, O_3, NO, NO, NO_2, ClO, - - - BrO$

36F, FO Exn with: $O, O_3, NO, NO_2, - - - FC$

37. ClOO Exn with: $Cl, - - - N$

37. OClO Exn with: $O, N, NO, N, Cl, - - -$

37F, FO₂ Exn with: O

38. ClO₃ Exn with:

39. HCl Exn with: $O, O(^1D), N, NO, - - -$

39Br, HBr Exn with: $O, NO, - - -$

39F, HF Exn with: $O(^1D)$

40. NOCl Exn with: $O, NO, - - -$

41. NOClO Exn with:

42. NOCl Exn with: $N, Cl, - - -$

43. NO₂Cl Exn with: $Cl, - - -$

58. C_2H_6 Hex with: O, $C(^1D)$, NO, NO_2 , Cl - - -

59. C_3H_6 Hex with: O, C_2 , NO - - -

100. C_3H_8 Hex with: O, NO, NO_2 - - -

100a. C_6H_6 Hex with: O, NO - - -

61. CF_2Cl_2 Hex with: O(1D), $O_2(^1\Delta)$, NO - - -

62. $CFCl_3$ Hex with: O(1D), NO - - -

63. CCl_4 Hex with: NO - - -

64. CH_2Cl_2 Hex with: O, $O_2(^1\Delta)$, O_3 , H, NO, Cl - - -

65. CH_2ClF_2 Hex with: O(1D), NO - - -

* and higher alkenes
† and higher alkanes
v and other aromatics
o and other halocarbons

PHOTOCHEMISTRY INDEX

| | | | | | |
|-----|-------------------------------|-----|--------------------|-----|-------------------------------------|
| 40 | 62 | 370 | Cl ₂ d | 530 | CH ₃ OH |
| 70 | 63 | 370 | Cl ₂ d | 540 | CH ₃ NO |
| 90 | NO | 380 | Cl ₂ d | 600 | CF ₃ Cl |
| 100 | NO ₂ | 390 | Cl ₂ d | 610 | CF ₂ Cl ₂ |
| 110 | NO ₃ | 390 | HF | 620 | CF ₂ Cl ₃ |
| 130 | N ₂ O | 400 | HCl | 630 | CCl ₄ |
| 140 | N ₂ O ₂ | 410 | HCl ₂ | 650 | CH ₂ Cl ₃ |
| 230 | N ₂ O ₂ | 420 | NOCl | 650 | CF ₂ d |
| 250 | NO ₂ | 430 | ClNO ₂ | 650 | CFCl ₂ |
| 260 | NO ₃ | 430 | ClNO ₂ | 650 | CCl ₂ d |
| 280 | NO ₄ | 430 | NO ₂ Cl | 650 | CCl ₂ CF ₃ |
| 280 | NO ₂ | 430 | NO ₂ Br | 650 | CCl ₂ CF ₂ Cl |
| 340 | CO ₂ | 440 | Cl ₂ | 650 | CCl ₂ CFCl ₂ |
| 360 | Cl ₂ | 460 | CH ₂ d | | |

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Temp. Range/K | Reaction Rate Constant $\text{L}/\text{cm}^3 \text{molecule}^{-2} \text{s}^{-1}$ | Uncert. Factor at 298K, notes |
|------|--|------------------|---|----------------------------------|
| 1.1M | $\text{O} + \text{O} + \text{M} \rightarrow \text{O}_2 + \text{M}$ | | $\Delta E (298) = -498 \text{ kJ/mol}$ | |
| | *Campbell, Gray (1973) | 200-300 | $4.6 \times 10^{-33} (\text{T}/300)^{-2}$ | M = N ₂ 1.3 |
| | *Baulch, et al (1976) review | 190-4000 | $5.2 \times 10^{-35} \exp(900/\text{T})$ | M = Ar 1.3 |
| | Johnston (1968) review | 1000-8000 | $3.80 \times 10^{-30} \text{T}^{-1} \exp(-170/\text{T})$ | M = O ₂ |
| | Taylor (1975) review | 2000-10000 | $1.7 \times 10^{-32} \text{T}^{-1/2}$ | M = N ₂ |
| | | | $2.2 \times 10^{-28} \text{T}^{-3/2}$ | M = O ₂ |
| | | | $6.2 \times 10^{-28} \text{T}^{-3/2}$ | M = H |
| | | | $8.2 \times 10^{-33} \text{T}^{-1/2}$ | M = N, NO |

This evaluation accepts the results of Campbell and Gray (1973) at low temperature and with $M = N_2$ as most applicable to stratospheric chemistry and also accepts the recent recommendation of Gaulch, et al (1976) for an extended temperature range with $M = Ar$.

REFERENCES

- Baulch, D. L., Drysdale, D. D., Duxbury, J., and Grant, S. J., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 3: Homogeneous Gas Phase Reactions of the O_2 - O_3 System, the CO - O_2 - H_2 System, and of Sulphur-Containing Species," (Butterworths, London, 1976)
- Campbell, I. M., and Gray, C. M., "Rate Constants for $O(^3P)$ Recombination and Association with $N(^4S)$," Chem. Phys. Lett. 18, 607-609 (1973)
- Johnston, H. S., "Gas Phase Reaction Kinetics of Neutral Oxygen Species," NBS-NBSDS-20, 1968. (Supe. of Documents, U.S. Govt. Printing Office, Washington, D.C. 20402)
- Taylor, R. L., "High Temperature Reactions of Air" pages 5-154 to 5-157 in "The Natural Stratosphere of 1974" Climatic Impact Assessment Program Monograph 1. D67-JST-75-51, Department of Transportation, Washington D.C., September 1975
- R. F. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No | Reaction/Reference | Temp Range/K | Reaction Rate Constant k/cm ³ molecule ⁻² s ⁻¹ | Uncert Factor at 298K, notes |
|--------------|---|--|---|---------------------------------|
| 1.4M 7.1M | $O(^3P) + O_2 \rightarrow M \rightarrow O_3 + M$ (f) $O_3 + M \rightarrow O + O_2 + M$ (r) NASA (1979) eval CODATA (1979) eval | 200-300 220-300 298 219-368 219-368 219-368 262-308 262-318 263-298 300 200-1000 200-1000 | ΔH (298) = -106 kJ/mol $k_f = (6.2 \pm 0.9) \times 10^{-34} (T/300)^{-2.0 \pm 0.5}$, M = N ₂ $k_r = 5-6 \times 10^{-34} (T/300)^{-2.4}$, M = N ₂ $k_f = 2.8 \times 10^{-12}$ cm ³ molecule ⁻¹ s ⁻¹ $k_r = (6.2 \pm 0.9) \times 10^{-34} (T/300)^{-2.0 \pm 0.5}$, M = N ₂ $k_f = (6.9 \pm 1.0) \times 10^{-34} (T/300)^{-1.25 \pm 0.2}$, M = O ₂ $k_r = (3.9 \pm 0.5) \times 10^{-34} (T/300)^{-1.9 \pm 0.3}$, M = Ar $k_f = 1.8 \times 10^{-35}$ exp(995/T), M = N ₂ $k_r = 6-8 \times 10^{-35}$ exp(635/T), M = O ₂ $k_f = 6-2 \times 10^{-35}$ exp(525/T), M = Ar $k_f = 5.5 \times 10^{-34}$ M = N ₂ $k_r = 4.1 \times 10^{-10}$ exp(-11430/T) cm ³ molecule ⁻¹ s ⁻¹ , M = Ar $k_f = 4-6 \times 10^{-35}$ exp(1050/T), M = Ar $k_r = 1-65 \times 10^{-9}$ exp(-11400/T) cm ³ molecule ⁻¹ s ⁻¹ Relo, M eff: O ₂ (1.0), Ar(0.25), O ₂ (0.44), N ₂ (0.39) $k_f = 6-6 \times 10^{-35}$ exp(510/T) M = Ar Relo, M efficiencies: Ar(1.0), He(0.9), N ₂ (1.7) $k_f = 4-7 \times 10^{-35}$ exp(840/T) M = Ar Relo, M eff: Ar(1.0), He(0.8), CO ₂ (3.4), O ₂ (1.1) $k_f = 1-0 \times 10^{-33}$ M = CO ₂ Relo, M eff: CO ₂ (1.0), CO(0.44), N ₂ O(0.88) $k_f = 5-4 \times 10^{-34}$ M = N ₂ Relo, M efficiencies: N ₂ (1.0) O ₂ (1.18), CO(1.24) $k_f = 5-0 \times 10^{-34}$ M = Ar Relo, M efficiencies: Ar(1.0), Kr(0.98), He(0.92) $k_f = 8 \times 10^{-34}$ M = N ₂ $k_f = 4-4 \times 10^{-34}$ M = Ar, Rel. eff. Ar(1.0), N ₂ (1.6) $k_f = 1-24 \times 10^{-34}$ M = O ₂ $k_f = 2-28 \times 10^{-34}$ M = Ar $k_f = 5-4 \pm 1-2 \times 10^{-34}$ M = N ₂ Relo, efficiencies: N ₂ (1.0), O ₂ (1.09), Ar(0.76) $k_f = 8 \times 10^{-34}$ M = N ₂ (a) $k_f = 2.8 \times 10^{-12}$ cm ³ molecule ⁻¹ s ⁻¹ (a) (a) Reevaluation of work in Hippler, Tree (1971) 6.3 x 10 ⁻³⁴ M = O ₂ | 1.3 3 |
| | Klaas, et al (1979) | | | |
| | Arnold, Comes (1979) | | | |
| | Baulch, et al (1976) review | | | |
| | Johnston (1968) eval | | | |
| | Hule, Herron, Davis (1972) | | | |
| | Mulcahy, Williams (1968) | | | |
| | Neuburn, et al (1968) | | | |
| | Stuhl, Miki (1971) | | | |
| | Donovan, Husain, Kirsch (1970) | | | |
| | Hippler, Tree (1971) | | | |
| | Slanger, Black (1970) | | | |
| | Francis (1969) | | | |
| | Sauer (1967) | | | |
| | Ball and Larkin (1973) | | | |
| | Hippler, Schieppert, Tree (1975) | | | |
| | Hogan, Dorch (1976) | | | |

REFERENCES

- Arnsfeld, I., and Cones, P. J., "Temperature Dependence of the Reactions $O(^3P) + O_3 \rightarrow 2O_2$ and $O(^3P) + O_2 + M \rightarrow O_3 + M$," *Chem. Phys. Lett.* 231-235 (1979)
- Bell, M. J., and Larkin, G. M., "Determination of the Rates of Atomic Reactions by the Discharge-Flow Method," *Nature Phys. Sci.* 245, 63-64 (1973)
- Baulch, B. L., Drysdale, B. D., Duxbury, J., and Grant, G. J., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 3: Homogeneous Gas Phase Reactions of the O_2-O_3 System, the $CO-O_2-H_2$ System, and of Sulphur-Containing Species," (Butterworths, London, 1976)
- COBATA(1979), Recommendations of the COBATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.
- Bonovan, M. J., Rusin, D., and Kirach, L. J., "Reactions of Atomic Oxygen, Part 1: The Rate of the Reaction $O + O_2 + M \rightarrow O_3 + M$ ($M = He, Ar$ and Kr)," *Trans. Faraday Soc.* 66, 2551-2559 (1970)
- Francis, P. D., "The Production of Oxygen Atoms in a Microwave Discharge and the Recombination Kinetics in a Gas Flow System," *Brit. J. Appl. Phys.* 2, 1717-1730 (1969)
- Hippler, R., and Troe, J., "Rekombinationsbereich der Rekombination $O + O_2 \rightarrow O_3$," *Ber. Bunsenges. Physik. Chem.* 75, 27-32 (1971)
- Hippler, R., Schipper, C., and Troe, J., "Photolysis of NO_2 and Collisional Energy Transfer in the Reactions $O + NO \rightarrow NO_2$ and $O + NO_2 \rightarrow NO_3$," *Int. J. Chem. Kinet., Symp. No. 1*, 27-38 (1975)
- Hogan, L. G., and Burch, D. S., "A Measurement of the Rate Constant for the Reaction $O + O_2 \rightarrow O_3 + O_2$," *J. Chem. Phys.* 65, 894-900 (1976)
- Kuo, M. K., Herren, J. T., and Davis, D. D., "Absolute Rate Constants for the Reaction $O + O_2 + M \rightarrow O_3 + M$ over the Temperature Range 200-340°K," *J. Phys. Chem.* 76, 2653-2658 (1972)
- Johnston, H. S., "Gas Phase Reaction Kinetics of Neutral Oxygen Species," NBS-NBS-20, 1968, (Supt. of Documents, U.S. Govt. Printing Office, Washington, D.C. 20402)
- Klein, G., Anderson, P. C., and Kurylo, M. J., "A Reinvestigation of the Temperature Dependence of the Rate Constant for the Reaction $O + O_2 + M \rightarrow O_3 + M$ (for $M = O_2, N_2$ and Ar) by the Flash Photolysis Resonance Fluorescence Technique," typescript, National Bureau of Standards, Washington, D.C. (1979)
- Meaburn, G. M., Ferner, D., LeCalve, J., and Bourne, M., "A Pulsed-Radiolysis Study of Atomic Oxygen Reactions in the Gas Phase," *J. Phys. Chem.* 72, 3920-3925 (1968)

Bulcaby, M. P. P., and Williams, R. J., "Kinetics of Combination of Oxygen Atoms with Oxygen Molecules," Trans. Faraday Soc. **54**, 59-70 (1968)

NASA (1979), Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future."

R. D. Hudson and R. I. Reed, Editors, Dec. 1979 (report of the June 1979 Harpers Ferry Workshop).

Sauer, M. G., Jr., "A Pulse-Radiolysis Study of the Dependence of the Reaction of Atomic Oxygen with Oxygen on the Nature of the Third Body," J. Phys. Chem. **71**, 3311-3313 (1967)

Slanger, T. G., and Black, G., "Reaction Rate Measurements of $O(^3P)$ Atoms by Resonance Fluorescence. I. $O(^3P) + O_2 + M - O_3 + M$ and $O(^3P) + NO + M - NO_2 + M$," J. Chem. Phys. **53**, 3717-3721 (1970)

Stuhl, F., and Niki, S., "Measurements of Rate Constants for Termolecular Reactions of $O(^3P)$ with NO , O_2 , CO , N_2 , and CO_2 Using a Pulsed Vacuum-uv Photolysis-Chemiluminescent Method," J. Chem. Phys. **55**, 3943-3953 (1971)

R. F. Hudson
June 1979

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Temp. Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncert. Factor at 298K, notes |
|------|---|------------------|---|----------------------------------|
| 1,4M | $O + O_2 \rightarrow O_3^+ + M$ This survey Revan, Johnson (1973) | 300 300 | $\Delta H(298) = -106 \text{ kJ/mol}$ $4 \times 10^{-34} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1} \quad M = O_2$ $5.4 \times 10^{-34} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1} \quad M = O_2$ Rel. efficiencies: $O_2(1.0)$, $Ar(0.50)$, $N_2(2.4)$, $CO_2(2.5)$, $SF_6(5.7)$ | 1.5 (a) |
| | von Rosenbergs, Trainer (1974) | 300 | $3 \times 10^{-34} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1} \quad M = O_2, N_2$ (a) Vibrationally excited O_3 followed as fn. of time using abn. $250 < \lambda < 330 \text{ nm}$ (b) Vibrationally excited O_3 followed as fn. of time using i.e. emission at 9.6 and $14.3 \mu\text{m}$ Also see von Rosenbergs, Trainer (1975) | (b) |

recommended value averages the two reported experimental values

REFERENCE

- Bewan, P. L., and Johnson, G. R. A., "Kinetics of Ozone Formation in the Pulse Radiolysis of Oxygen Gas," J. Chem. Soc., Faraday Trans. I **69**, 216-227 (1973)
- von Rosenberg, C. W., Jr., and Trainor, D. W., "Vibrational Excitation of Ozone Formed by Recombination," J. Chem. Phys. **51**, 2442-2456 (1974)
- R. F. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Uncertainty Factor
at 298K, notes

| No. | Reaction/Reference | Temp. Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncertainty Factor at 298K, notes |
|-----|---|--|---|--------------------------------------|
| 1.7 | $O(^3P) + O_3 \rightarrow O_2 + O_2$ NASA (1979) eval CODATA (1979) eval Hampton (1973) eval Baulch, et al (1976) review McCrum, Kaufman (1972) Lundell, Ketcheson, Schiff (1969) Busala, Kirach, Donovan (1972) Davis, Wong, Lephardt (1973) | 200-300 220-1000 220-1000 200-500 269-409 300 300 220-353 | $\Delta H (298) = -392 \text{ kJ/mol}$ $1.5 \times 10^{-11} \text{ exp}(-22180/150)/T$ $2.0 \times 10^{-11} \text{ exp}(-2280/130)/T$ $1.9 \times 10^{-11} \text{ exp}(-2300/T)$ $8.6 \times 10^{-12} \text{ exp}(-2090/T)$ $1.1 \times 10^{-11} \text{ exp}(-2155/T)$ 1.5×10^{-14} 1.3×10^{-14} $2.0 \times 10^{-11} \text{ exp}(-2280/T)$ | 1.15 1.25 |

This recommendation is slightly different from the NBS SP 513 and NASA RP 1010 recommendation ($k = 1.9 \times 10^{-11} \text{ exp}(-2300/T)$) and is based on the measurements of McCrum and Kaufman (1972) and Davis et al (1973)

REFERENCES

- Baulch, D. L., Drysdale, D. D., Duxbury, J., and Grant, S. J., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 3: Homogeneous Gas Phase Reactions of the O_2 - O_3 System, the CO - O_2 - H_2 System, and of Sulphur-Containing Species," (Butterworths, London, 1976)
- CODATA(1979), Recommendations of the CODATA Task Group on Chemical Kinetics, To be published in the Journal of Physical and Chemical Reference Data.
- Davis, D. D., Wong, W., and Lephardt, J., "A Laser Flash Photolysis-Resonance Fluorescence Kinetic Study: Reaction of $O(^3P)$ with O_3 ," *Chem. Phys. Lett.*, **22**, 273-278 (1973)
- Hampton, R. F., (editor), "Survey of Photochemical and Rate Data for Twenty-Eight Reactions of Interest in Atmospheric Chemistry," *J. Phys. Chem. Ref. Data*, **2**, No. 2, 267-312 (1973). These are revised versions of data sheets originally distributed as NBS Reports 10692 and 10628.
- Hampton, R. F., and Garvin, D., "Reaction Rate and Photochemical Data for Atmospheric Chemistry-1977" U.S. National Bureau of Standards Special Publication 513, May 1978.
- Busala, D., Kirach, L. J., and Donovan, R. J., "A Kinetic Study of $O(^3P)$

- by Atomic Absorption Spectroscopy Following the Flash Photolysis of
Ozone," *J. Photochem.* **1**, 69-73 (1972)
- Lundell, G. R., Ketcheson, R. D., and Schiff, E. I., "The Production of $O(3P)$
Atoms, Free From Excited Molecules, and Their Reaction with O_3 ," *Symp.*
Combust, 12th (Combustion Institute, Pittsburgh, 1969) 397-311
- McCrush, J. L., and Kaufman, F., "Kinetics of the $O + O_3$ Reaction," *J. Chem.*
Phys. **52**, 1270-1276 (1972)
- NASA RP-1010, "Chlorofluoromethanes and the Stratosphere"
R. D. Hudson, Editor, August 1977 This reference contains
the NASA (1977) rate constant recommendations
NASA (1979). Recommendations of the NASA Panel for Data Evaluation,
published in NASA RP 1049 "The Stratosphere: Present and Future."
R. D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the
June 1979 Harpers Ferry Workshop).
- R. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Uncert. Factor
at 298K, notes

Reaction/Reference

Temp.
Range/K

Reaction Rate Constant
k/cm³molecule⁻¹s⁻¹

No

| | | | | |
|------|-----------------------------|------------------------|--|--|
| 1.0M | O + N + M → NO + M (2) | ΔH (298) = -632 kJ/mol | | |
| 9.0M | NO + N + O → M (2) | | | |
| | Baulch, et al (1973) review | | | |
| | | 200-400 | | |
| | | 4200-6700 | | |
| | Taylor (1975) | 2000-10000 | | |
| | Campbell, Gray (1973) | 298 | | |
| | | 196 | | |

This evaluation accepts the recommendations in the review of Baulch, et al (1973)

REFERENCES

- Baulch, D. L., Drysdale, D. D., and Horne, D. G., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 2: Homogeneous Gas Phase Reactions of the N₂-N₂-O₂ System," (Butterworths, London, 1973)
- Campbell, I. M., and Gray, C. No., "Rate Constants for O(3P) Recombination and Association with N(4S)," Chem. Phys. Lett. 18, 607-609 (1973)
- Taylor, R. L., "High Temperature Reactions of Air" pages 5-154 to 5-157 in "The Natural Stratosphere of 1974" Climatic Impact Assessment Program Monograph 1, DOT-TST-75-51, Department of Transportation, Washington D.C., September 1975

R. F. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Uncert. Factor
at 298K, notes

Reaction/Reference Temp.
Range/K Reaction Rate Constant
k/cm³molecule⁻¹s⁻¹

No.

| | | | |
|-----|-------------------------------|-----|-------------------------|
| 1.9 | O + NO → NO ₂ + hv | 300 | ΔH (298) = -306 kJ/mol |
| | Becker, et al (1973) | | 4.2 x 10 ⁻¹⁸ |

No recommendation

REFERENCES

Becker, K. E., Groth, W., and Threl, D., "Mechanism of the Air Afterglow
NO + O → NO₂ + hv," Symp. Combust. 14th (Combustion Institute,
Pittsburgh, 1973) 353-363

E. F. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No | Reaction/Reference | Temp. Range/K | Reaction Rate Constant $k/\text{cm}^6\text{molecule}^{-2}\text{s}^{-1}$ | Uncert. Factor at 298K, notes |
|------|--|------------------|---|----------------------------------|
| 1.9M | $\text{O} + \text{Mg} \rightarrow \text{M} + \text{Mg}_2 \rightarrow \text{M} (2)$ | | | |
| 1.9M | $\text{Mg}_2 \rightarrow \text{M} + \text{Mg} \rightarrow \text{O} + \text{M} (2)$ | | | |
| | NASA (1979) eval | 200-300 | $k_1 = (1.2 \pm 0.3) \times 10^{-31} (T/300)^{-1.8 \pm 0.5}, M = \text{N}_2$ $k_{1,0} = (3.0 \pm 1.0) \times 10^{-11} (T/300)^{0.3 \pm 1} \text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$ $k_2 = 1.2 \times 10^{-31} (T/300)^{-1.82}, M = \text{N}_2$ 1.3 $k_{2,0} = 3.0 \times 10^{-11} (T/300)^{0.3 \pm 1} \text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$ 1.6 $k_3 = 1.55 \times 10^{-32} \exp(584/T), M = \text{N}_2$ $k_4 = 1.18 \times 10^{-31} (T/300)^{-1.82}$ | |
| | CODATA (1979) eval | 200-300 | $k_2 = 3.0 \times 10^{-33} \exp(940/T), M = \text{O}_2$ | |
| | Whytock, Michael, Payne (1976) | 300-1500 | Rel. M efficiencies: $\text{O}_2(1.0), \text{Ar}(1.0), \text{N}_2(1.4)$ | |
| | Baulch, et al (1973) review | 200-500 | $k_2 = 1.8 \times 10^{-8} \exp(-33000/T) \text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$ $M = \text{Ar}$ | |
| | Slanger, Wood, Black (1973) | 296 | $k_2 = 6.0 \times 10^{-32} M = \text{Ar}$ | |
| | Hippler, Schipper, Troe (1975) | 241 | $k_2 = 13.0 \times 10^{-32} M = \text{Ar}$ | |
| | Atkinson, Pitts (1974) | 300-392 | $k_2 = 7.4 \times 10^{-32}, M = \text{N}_2$ $k_2(\infty) = 3.0 \times 10^{-11} \text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$ | |
| | Singh, Ion, et al (1975) | 298-473 | $k_2 = 2.6 \times 10^{-32} \exp(450 \pm 100/T) M = \text{N}_2\text{O}$ | |
| | Campbell, Bandy (1975) | 265-425 | $k_2 = 1.7 \times 10^{-32} \exp(620/T), M = \text{M}_2\text{O}$ | |
| | Michael, Payne, Whytock (1976) | 217-500 | $k_2 = 5.0 \times 10^{-33} \exp(900/T), M = \text{N}_2$ $k_2 = 1.06 \times 10^{-32} \exp(520/T), M = \text{He}$ $k_2 = 9.33 \times 10^{-23} \exp(515/T), M = \text{Ne}$ $k_2 = 9.01 \times 10^{-23} \exp(590/T), M = \text{Ar}$ $k_2 = 9.52 \times 10^{-23} \exp(570/T), M = \text{Kr}$ | |

Recommendation for k_2 based on results of Whytock et al (1976),
Recommendation for $k_{1,0}$ based on results of Hippler et al (1975).

REFERENCES

- Atkinson, R., and Pitts, J. N., Jr., "Rate Constants for the Reaction of
 $\text{O}(^1\text{P})$ Atoms with $\text{Mg}_2 (M = \text{N}_2\text{O})$ over the Temperature Range 299-392 K,"
Chem. Phys. Lett. **29**, 28-30 (1974)
- Baulch, D. L., Drysdale, D. D., and Horne, D. G., "Evaluated Kinetic
Data for High Temperature Reactions, Vol. 2: Homogeneous Gas
Phase Reactions of the $\text{M}_2\text{-M}_2\text{-O}_2$ System," (Butterworths, London, 1973)

- Campbell, I. M., and Randy, R. J., "Studies of Reactions of Atoms in a Discharge Flow Stirred Reactor Part I - The $O + H_2 + NO$ System," *J. Chem. Soc., Faraday Trans. 1*, 21, 2097-2106 (1975)
 CODATA(1979), Recommendations of the CODATA Task Group on Chemical Kinetics, To be published in the Journal of Physical and Chemical Reference Data.
- Hippler, R., Schipper, C., and Iroe, J., "Photolysis of NO_2 and Collisional Energy Transfer in the Reactions $O + NO \rightarrow NO_2$ and $O + NO_2 \rightarrow NO_3$," *Int. J. Chem. Kinet.*, Symp. No. 1, 27-38 (1975)
- Michael, J. V., Payne, W. A., and Whyteck, D. A., "Absolute Rate Constants for $O + NO + M (-He, Ne, Ar, Kr) \rightarrow NO_2 + M$ from 217 to 500 K," *J. Chem. Phys.* **65**, 4830-4834 (1976)
- Slanger, T. G., Wood, R. J., and Black, G., "Investigation of the Rate Coefficient for $O(^3P) + NO_2 \rightarrow O_2 + NO$," *Int. J. Chem. Kinet.* **5**, 615-620 (1973)
- NASA (1979), Recommendations of the NASA Panel for Data Evaluation, published in NASA SP 1049 "The Stratosphere: Present and Future," R. D. Hudson and R. L. Reed, Editors, Dec, 1979 (report of the June 1975 Harpers Ferry Workshop).
- Singleton, D. L., Furuyama, S., Cveticovic, E. J., and Irwin, R. S., "Temperature Dependence of the Rate Constants for the Reactions $O(^3P) + 2,3$ -Dimethyl-2-Butene and $O(^3P) + NO + M$ Determined by a Phase Shift Technique," *J. Chem. Phys.* **63**, 1003-1007 (1975)
- Whyteck, D. A., Michael, J. V., and Payne, W. A., "Absolute Rate Constants for $O + NO + M_2 \rightarrow NO_2 + M_2$ from 217 - 500 K," *Chem. Phys. Lett.* **42**, 466-471 (1976)
- R. F. Hampson
 June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Temp. Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncert. Factor at 298K, notes |
|------|---|------------------|--|----------------------------------|
| | | | | |
| 1.9M | O + NO + M → NO ₂ + M + hv Becker, et al (1973) | 300 | ΔH (298) = -306 kJ/mol 7 × 10 ⁻³² cm ⁶ molecule ⁻² s ⁻¹ | |

No recommendation

REFERENCES

Becker, K. H., Groth, W., and Thran, D., "Mechanism of the Air Afterglow
NO + O → NO₂ + hv," Symp. Combust. 14th (Combustion Institute,
Pittsburgh, 1973) 353-363

R. F. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Temp. Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncert. Factor at 298K, notes |
|------|--|------------------|--|----------------------------------|
| 1.10 | $O(^3P) + NO_2 \rightarrow NO + O_2$ (2) | | | |
| 4.9 | $O_2 + NO \rightarrow NO_2 + O$ (r) | | | |
| | NASA (1979) | | | |
| | CODATA (1979) | | | |
| | Davis, Herron, Hule (1973) | | | |
| | Baulch, et al (1973) review | | | |
| | Clyne, Cruse (1971) | | | |
| | Harker, Johnston (1973) | | | |
| | Clyne, Cruse (1972) | | | |
| | Slanger, et al (1973) | | | |
| | Stuhl, Niki (1970) | | | |
| | Bemand, Clyne, Watson (1974) | | | |
| | | 200-300 | $k_f = 9.3 \times 10^{-12}$ | 1.1 |
| | | 230-340 | $k_f = 9.3 \times 10^{-12}$ | 1.15 |
| | | 230-339 | $k_f = 9.1 \times 10^{-12}$ | |
| | | 300-550 | $k_f = 1.7 \times 10^{-11} \exp(-300/T)$ | |
| | | | $k_r = k_f/K_{eq} = 2.8 \times 10^{-12} \exp(-23400/T)$ | |
| | | 300 | $k_f = 8.3 \times 10^{-12}$ | (a) |
| | | 300 | $k_f = 9.2 \times 10^{-12}$ | (b) |
| | | 298 | $k_f = 6.1 \times 10^{-12}$ | (b) |
| | | 300 | $k_f = 9.3 \times 10^{-12}$ | (b) |
| | | 240 | $k_f = 10.5 \times 10^{-12}$ | (b) |
| | | 300 | $k_f = 4.4 \times 10^{-12}$ | (c) |
| | | 230-1055 | $k_f = 1.75 \times 10^{-10} \times (T)^{-0.52}$ | |
| | | 298 | $k_f = 9.54 \times 10^{-12}$ | |

(a) $k/k(O + NO \rightarrow N)$ measured, where $k(\text{ref}) = 6.9 \times 10^{-32}$

(b) Similar techniques were used by Slanger and by Stuhl and Niki: Flash Photolysis - chemiluminescence.

(c) Based on this work (298 $^{\circ}K$ 1055) and other recent work.

Based on results of Davis et al (1973), Bemand et al (1974) and Slanger et al (1973). There may be a slight negative temperature coefficient, but the evidence at low temperature is uncertain. A slightly lower value was recommended in NASA RP-1010 based only on the results of Davis et al (1973)

REFERENCES

- Baulch, D. L., Drysdale, D. D., and Horne, D. G., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 2: Homogeneous Gas Phase Reactions of the H_2 - N_2 - O_2 System," (Butterworths, London, 1973)
- Bemand, P. P., Clyne, M. A. A., and Watson, R. T., "Atomic Resonance Fluorescence and Mass Spectrometry for Measurements of the Rate Constants for Elementary Reactions: $O(^3P) + NO_2 \rightarrow NO + O_2$ and $NO + O_3 \rightarrow NO_2 + O_2$," J. Chem. Soc., Faraday Trans. II **70**, 564-576 (1974)
- Clyne, M. A. A., and Cruse, H. W., "Studies of Ground-State $P_{3/2}$ Halogen Atoms Using Atomic Resonance Absorption," Trans. Faraday Soc. **67**, 2669-2685 (1971)
- Clyne, M. A. A., and Cruse, H. W., "Atomic Resonance Fluorescence Spectrometry for Rate Constants of Rapid Bimolecular Reactions, Part 1. Reactions $O + NO_2$, $Cl + ClNO$, $Br + ClNO$," J. Chem. Soc., Faraday Trans. II **68**, 1281-1299 (1972)
- CODATA(1979), Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.
- Devils, D. D., Herroon, J. T., and Eule, R. E., "Absolute Rate Constants for the Reaction $O(^3P) + NO_2 \rightarrow NO + O_2$ over the Temperature Range 230-339K," J. Chem. Phys. **58**, 530-535 (1973)
- Harker, A., and Johnston, H. S., "Photolysis of Nitrogen Dioxide to Produce Transient O , NO_3 and N_2O_5 ," J. Phys. Chem. **77**, 1153-1156 (1973)
- NASA RP-1010, "Chlorofluoromethanes and the Stratosphere" R. D. Hudson, Editor, August 1977 This reference contains the NASA (1977) rate constant recommendations.
- NASA (1979), Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," R. D. Hudson and E. L. Reed, Editors, Dec. 1979 (report of the June 1979 Harpers Ferry Workshop).
- Slanger, T. G., Wood, B. J., and Black, G., "Investigation of the Rate Coefficient for $O(^3P) + NO_2 \rightarrow O_2 + NO$," Int. J. Chem. Kinet. **5**, 615-620 (1973)
- Stuhl, F., and Miki, E., "Detection of Oxygen (3P) Atoms in Pulsed Vacuum UV Photolysis of NO and Its Application to O Atom Reactions," Chem. Phys. Lett. **7**, 157-200 (1970)
- W. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No | Reaction/Reference | Temp Range/K | Reaction Rate Constant k/cm ⁶ molecule ⁻² s ⁻¹ | Uncert Factor at 298K, notes |
|-------|---|--------------|--|---------------------------------|
| 1,1,M | O + NO ₂ → N + NO ₃ + M (1) | | ΔH (298) = -210 kJ/mol | |
| 11,M | NO ₃ + N → NO ₂ + O + M (r) | | | |
| | NASA (1979) eval | 200-300 | $k_1 = (9.0 \pm 1.0) \times 10^{-32} (T/300)^{-2.0 \pm 1.0}$, M = N ₂ $k_{1a} = (2.0 \pm 0.3) \times 10^{-11}$ cm ³ molecule ⁻¹ s ⁻¹ | |
| | CODATA (1979) eval | 298 | $k_1 = 9 \times 10^{-32}$, M = N ₂ $k_{1a} = 2.0 \times 10^{-11}$ cm ³ molecule ⁻¹ s ⁻¹ | 1.3 |
| | Rampson, et al (1973a) review | 298 | $k_1 = 1.0 \times 10^{-31}$, M = N ₂ | 1.3 |
| | Baulch, et al (1973) review | 295 | $k_1 = 6.3 \times 10^{-32}$, M = N ₂ $k_2 = 8 \times 10^{-42}$ cm ³ molecule ⁻¹ s ⁻¹ , $k_2 = k_1/K_{eq}$ | |
| | Hippler, Schipper, Troe (1975) | 300 | $k_1 = 8.0 \times 10^{-32}$, M = N ₂ $k_2(-) = 2.0 \times 10^{-11}$ cm ³ molecule ⁻¹ s ⁻¹ | |
| | Harker, Johnston (1973) | 297 | $k_1 = 8.2 \times 10^{-32}$, M = N ₂ | |

Recommended values based on results of Harker and Johnston (1973) and Hippler et al (1975)

REFERENCES

- Baulch, D. L., Drysdale, D. D., and Horne, D. G., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 2: Homogeneous Gas Phase Reactions of the H₂-N₂-O₂ System," (Butterworths, London, 1973)
- CODATA(1979), Recommendations of the CODATA Task Group on Chemical Kinetics: To be published in the Journal of Physical and Chemical Reference Data.
- Rampson, E. F., (editor), "Chemical Kinetics Data Survey VI: Photochemical and Rate Data for Twelve Gas Phase Reactions of Interest for Atmospheric Chemistry," NBSIR 73-207 (1973a)
- Harker, A., and Johnston, E. S., "Photolysis of Nitrogen Dioxide to Produce Transient O, NO₃ and F₂O₅," J. Phys. Chem. **77**, 1153-1156 (1973)
- Hippler, E., Schipper, U., and Troe, J., "Photolysis of NO₂ and Collisional Energy Transfer in the Reactions O + NO → NO₂ and O + NO₂ → NO₃," Int. J. Chem. Kinet., Sympo No. 1, 27-38 (1975)
- NASA (1979), Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," E. D. Hudson and E. L. Reed, Editors, Dec. 1979 (report of the June 1975 Harpers Ferry Workshop)
- E. F. Rampson
June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Temp. Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncert. Factor at 298K, notes |
|------|--|------------------|--|----------------------------------|
| 1.11 | O + NO ₃ → O ₂ + NO ₂ | | ΔH (298) = -287 kJ/mol | |
| | NASA (1979) eval | 200-300 | 1 × 10 ⁻¹¹ exp((0.150)/T) | 1.6 |
| | CODATA (1979) eval | 298 | 1 × 10 ⁻¹¹ | 3 |
| | Graham, Johnston (1978) | 298-329 | (1.0 ± 0.4) × 10 ⁻¹¹ | |

Based on study of Graham and Johnston (1978) and 298 K and 329 K, while limited in temperature range, the data indicate no temperature dependence. Furthermore by analogy with the reaction of O with NO₂ it is assumed that this rate constant is in fact independent of temperature. Clearly, temperature dependent studies are needed

REFERENCES

CODATA(1979). Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.

Graham, R. A., and Johnston, H. S., "The Photochemistry of NO₃ and the Kinetics of the N₂O₅-O₃ System," J. Phys. Chem. 82, 254-268 (1978)
NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future,"
R. D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the June 1979 Harpers Ferry Workshop).

R. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Temp. Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncertainty Factor at 298K, notes | |
|-------|---|------------------|--|---|------------------|
| | | | | | |
| 1.12M | O + N ₂ → N + N ₂ O + N (x) | | ΔH (298) = -167 kJ/mol | | |
| 13. M | N ₂ O + N → N ₂ + O + N (r) | | | | |
| | Baulch, et al (1973) review | 1300-2500 | k _f = 3.9 x 10 ⁻³⁵ exp(-10400/T) cm ⁶ molecule ⁻² s ⁻¹ M = Ar k _r = 8.3 x 10 ⁻¹⁰ exp(-29000/T) cm ³ molecule ⁻¹ s ⁻¹ M = Ar | 10 ⁵ (a) | |
| | | 900-2100 | k _f = 5.9 x 10 ⁻¹⁵ exp(-11330/T) cm ³ molecule ⁻¹ s ⁻¹ k _r = 1.3 x 10 ⁻¹¹ exp(-30000/T)s ⁻¹ (a) k _f = k _r K _{eq} (b) 2d order high pressure limit (c) 1st order high pressure limit | 10 ⁵ 10 ⁵ (a,b) 10 ⁵ (c) | |
| | Schofield (1973) review | 300-566 | k _f = 5 x 10 ⁻³⁸ cm ⁶ molecule ⁻² s ⁻¹ | | upper limit only |
| | | 800-2100 | k _r = 1.4 x 10 ¹¹ exp(-30,000/T)s ⁻¹ | | 1st order limit |

This evaluation accepts the recommendations in the review of Baulch, et al (1973)

REFERENCES

- Baulch, D. L., Drysdale, D. D., and Horne, D. G., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 2: Homogeneous Gas Phase Reactions of the H₂-N₂-O₂ System," (Butterworths, London, 1973)
- Schofield, K., "Evaluated Chemical Kinetic Rate Constants for Various Gas Phase Reactions," J. Phys. Chem. Ref. Data 2, 25-84 (1973)

Y. F. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Temp. Range/K | Reaction Rate Constant $k/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$ | Uncert. Factor at 298K, notes |
|------|--|------------------|---|----------------------------------|
| 1.13 | $\text{O} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{O}_2$ (1) | | ΔH (298) = -331 kJ/mol | |
| 4.12 | $\text{O}_2 + \text{H}_2 \rightarrow \text{O} + \text{H}_2\text{O}$ (1r) | | | |
| 1.13 | $\text{O} + \text{H}_2\text{O} \rightarrow \text{HO} + \text{HO}$ (2) | | = -151 kJ/mol | |
| 9.9 | $\text{HO} + \text{HO} \rightarrow \text{H}_2\text{O} + \text{O}$ (2r) | | | |
| | Baulch, et al (1973) review | 1200-2000 | $k_1 = 1.7 \times 10^{-10} \exp(-14100/T)$ $k_{1r} = 1.0 \times 10^{-10} \exp(-55200/T)$ (a) $k_f = k_r K_{eq}$ $k_2 = 1.7 \times 10^{-10} \exp(-14100/T)$ $k_{2r} = 2.2 \times 10^{-12} \exp(-32100/T)$ $k_{2f} = 0.4T^{-5/2} \exp(-43000/T)$ | 2.5 2.5 (a) 2 2 |
| | Taylor (1975) review | 2000-10000 | | |

This evaluation accepts the recommendations in the review of Baulch, et al (1973)

REFERENCES

- Baulch, D. L., Drysdale, D. B., and Horne, D. G., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 2: Homogeneous Gas Phase Reactions of the H_2 - H_2 - O_2 System," (Butterworths, London, 1973)
- Taylor, R. L., "High Temperature Reactions of Air" pages 5-154 to 5-157 in "The Natural Stratosphere of 1974" Climatic Impact Assessment Program Monograph 1, DGT-TST-75-51, Department of Transportation, Washington D.C., September 1975

P. F. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No | Reaction/Reference | Temp. Range/K | Reaction Rate Constant $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | Uncert. Factor at 298K, notes |
|------|---|------------------|--|----------------------------------|
| 1.14 | $\text{O} + \text{H}_2\text{O}_2 \rightarrow \text{products}$ | | | |
| | NASA (1979) eval | 298 | $< 3 \times 10^{-16}$ | |
| | CODATA (1979) eval | 220-300 | $< 3 \times 10^{-16}$ | |
| | Kaiser, Japar (1978) | 223, 300 | $< 3 \times 10^{-16}$ | |
| | Graham, Johnston (1978) | 300 | $< 2 \times 10^{-14}$ | |

This recommendation is based on the upper limit reported by Kaiser and Japar (1978)

REFERENCES

CODATA(1979), Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.

Graham, R. A., and Johnston, R. E., "The Photochemistry of NO_3 and the Kinetics of the $\text{H}_2\text{O}_2\text{-O}_3$ System," J. Phys. Chem. **82**, 254-268 (1978)

Kaiser, E. V., and Japar, V. M., "The Kinetics of the Gas Phase Reaction of $\text{O}(\text{P})$ with H_2O_2 ," Chem. Phys. Lett., **24**, 265-268 (1978)

NASA (1979), Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," R. D. Hudson and E. L. Reed, Editors, Dec. 1979. (report of the June 1979 Harpers Ferry Workshop).

E. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY
 PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Temp. Range/K | Reaction Rate Constant $k/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$ | Uncert. Factor at 298K, notes |
|------|---|------------------|--|----------------------------------|
| 1.16 | $\text{O} + \text{NH}_2 \rightarrow \text{NH} + \text{H}$ (a) $\rightarrow \text{HO} + \text{NH}$ (b) Gehring, et al (1973) | 300 | $\Delta H(298) = -116 \text{ kJ/mol}$ $= -52 \text{ kJ/mol}$ $3.5 \times 10^{-12} (k_a + k_b)$ | |

Only reported value - no recommendation

REFERENCES

Gehring, M., Hoyermann, K., Schacke, H., and Wolfrum, J., "Direct Studies of Some Elementary Steps for the Formation and Destruction of Nitric Oxide in the H-N-O System," Symp. Combust. 14th (Combustion Institute, Pittsburgh, 1973) 59-105

D. F. Haysdon
 May 1978

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Temp. Range/K | Reaction Rate Constant $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | Uncertainty Factor at 298K, notes |
|-------|--|------------------|--|--------------------------------------|
| 1.17 | $\text{O} + \text{NH}_3 \rightarrow \text{HO} + \text{NH}_2$ (1) | | | |
| 16.19 | $\text{HO} + \text{NH}_2 \rightarrow \text{O} + \text{NH}_3$ (r) | | | |
| | Baulch, et al (1973) review | | | |
| | | 300-1000 | $k_1 = 2.5 \times 10^{-12} \exp(-3020/T)$ | 1.5 |
| | | 300-1000 | $k_2 = k_1/K_{\text{eq}} = 1 \times 10^{-13}$ | 1.5 (a) |
| | Kurylo, et al (1969) | 361-677 | $k_1 = 6.6 \times 10^{-12} \exp(-3300/T)$ | |
| | Albers, et al (1969) | 300-1000 | $k_1 = 2.5 \times 10^{-12} \exp(-3020/T)$ | |
| | Kondratiev (1970) review | 350-1000 | $k_1 = 1.8 \times 10^{-12} \exp(-2500/T)$ | |
| | | | (a) $\text{HO} + \text{NH}_2 \rightarrow \text{NH} + \text{H}_2\text{O}$ may be preferred channel. | |

This evaluation accepts the recommendations in the review of Baulch, et al (1973)

REFERENCES

- Albers, E. A., Heyermann, L., Wagner, E. G., and Wolfrum J., "Study of the Reaction of Ammonia with Oxygen Atoms," *Symposium on Combustion*, 12th (Combustion Institute, Pittsburgh, 1969) 313-321
- Baulch, D. L., Drysdale, D. D., and Horne, D. G., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 2: Homogeneous Gas Phase Reactions of the H_2 - N_2 - O_2 System," (Butterworths, London, 1973)
- Kondratiev, V. N., "Konstanty Skorosti Gazofaznykh Reaktsiy Spravochnik," (Izdatelstvo "Nauka", Moskva, 1970); also issued as "Rate Constants of Gas Phase Reactions, Reference Book," E. M. Fristrom, Ed., Translated by L. J. Holtschlag CCM-72-10014, Office of Standard Reference Data, NBS (1972) (Distributed by National Technical Information Service, Springfield, Va. 22151)
- Kurylo, M. J., Hollinden, G. A., LeFevre, R. F., and Timmons, R. E., "ESR Study of the Kinetics of the Reactions of D Atoms and O Atoms with NH_3 ," *J. Chem. Phys.* **51**, 4497-4501 (1969)
- R. F. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Uncert. Factor
at 298K, notes

Reaction Rate Constant
 $\text{m}^3/\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$

Temp.
Range/K

Reaction/Reference

No.

| | | | | |
|-------|---|---|-----------------|----|
| 1,18M | $\text{O} + \text{H} + \text{M} \rightarrow \text{HO} + \text{M} (2)$ | $\Delta H (298) = -428 \text{ kJ/mol}$ | | |
| 19, M | $\text{HO} + \text{M} \rightarrow \text{H} + \text{O} + \text{M} (2)$ | $k_f \sim 2 \times 10^{-32} \text{ cm}^6 \text{ molecule}^{-2} \text{s}^{-1}$ | $M = \text{Ar}$ | 10 |
| | Schofield (1973) review | No recommendation for k_f or k_p | | |
| | Baulch, et al (1972) review | | | |

This evaluation accepts the recommendation for k_f given in the review of Schofield (1973).
No recommendation for k_p but note that $E/R > 50000 \text{ K}$

REFERENCES

Baulch, D. L., Drysdale, D. D., Horne, D. G., and Lloyd, A. G., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 1: Homogeneous Gas Phase Reactions of the $\text{H}_2\text{-O}_2$ System," (Butterworths, London, 1972)
Schofield, K., "Evaluated Chemical Kinetic Rate Constants for Various Gas Phase Reactions," J. Phys. Chem. Ref. Data 2, 25-84 (1973)

R. F. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Temp. Range/K | Reaction Rate Constant $k/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$ | Uncert. Factor at 298K, notes |
|------|---|------------------|--|----------------------------------|
| 1.19 | $\text{O} + \text{H}_2 - \text{H} + \text{O}_2 (x)$ | | $\Delta H (298) = -70 \text{ kJ/mol}$ | |
| 4.18 | $\text{O}_2 + \text{H} - \text{O} + \text{H}_2 (r)$ | | | 1.5 |
| | NASA (1979) eval | 200-300 | $k_f = 4 \times 10^{-11} \exp((0.3300)/T)$ | 2 |
| | CGDATA (1979) eval | 298 | $k_f = 3.8 \times 10^{-11}$ | |
| | Kaufman (1964) | 310 | $k_f = (5 \pm 2) \times 10^{-11}$ | |
| | Clyne (1963) | 265, 293 | $k_f = (5 \pm 2) \times 10^{-11}$ | |
| | Westenberg et al (1970) | 228-340 | $k_f = (3.2 \pm 0.5) \times 10^{-11}$ | |
| | Wilson (1972) review | 300-2000 | $k_f = (4.2 \pm 1.7) \times 10^{-11}$ | |
| | Baulch, et al (1972) review | 300 | $k_f = (3.8 \pm 1.7) \times 10^{-11}$ | |
| | Baulch, et al (1972) review | 700-2500 | $k_f = 3.7 \times 10^{-10} \exp(-8450/T)$ | |

This value is based on the work of Kaufman (1964), Clyne (1963) and Westenberg et al (1970)

REFERENCES

- Baulch, D. L., Drysdale, D. D., Horne, D. G., and Lloyd, A. C., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 1: Homogeneous Gas Phase Reactions of the $\text{H}_2\text{-O}_2$ System," (Butterworths, London, 1972)
- Clyne, M. A. A., "Rates of Some Atomic Reactions Involving Hydrogen and Oxygen," Symp. Combust. 9th (Academic Press, New York, 1963) 211-219
- CGDATA(1979), Recommendations of the CGDATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.
- Kaufman, F., "Aeronomomic Reactions Involving Hydrogen

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Temp. Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncertainty Factor at 298K, notes |
|-------|---|------------------|--|--------------------------------------|
| 1,19M | $O + H_2 \rightarrow H_2O + M$ (f) | | $\Delta H (298) = -286 \text{ kJ/mol}$ | |
| 20,M | $H_2O_2 + M \rightarrow H_2O + H_2O + M$ (r) Baulch, et al (1972) review | | no recommendation for forward or reverse rxn | |

See the review of Baulch, et al (1972) for a discussion of reported results. However, because of an insufficient data base, no recommendation can be made

REFERENCES

Baulch, D. L., Drysdale, D. D., Horne, D. G., and Lloyd, A. G. "Evaluated Kinetic Data for High Temperature Reactions, Vol. 1: Homogeneous Gas Phase Reactions of the H₂-O₂ System." (Butterworths, London, 1972)

P. F. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Temp. Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncert. Factor at 298K, notes |
|------|--|------------------|--|----------------------------------|
| 1.20 | O + H ₂ - H ₂ + O ₂ | | | |
| | NASA (1979) eval | 200-300 | $3.5 \times 10^{-11} \exp((0.350)/T)$ | 1.5 |
| | CODATA (1979) eval | 298 | 3.1×10^{-11} | 3 |
| | Burrows, Harris, Thrush (1977) | 293 | 3.5×10^{-11} (a) Based on value for k(O + H ₂) and k(H ₂ + H ₂ O ₂) | (a) |

$\Delta H(298) = -212 \text{ kJ/mol}$

This is the recent measurement of Burrows et al (1977). There are no T dependence data

REFERENCES

Burrows, J. P., Harris, G. W., and Thrush, B. A., "Rates of Reaction of H₂ with H₂ and O studied by Laser Magnetic Resonance," Nature **267**, 233-234 (1977)

CODATA(1979). Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.

NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA EP 1049 "The Stratosphere: Present and Future," R. D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the June 1979 Harpers Ferry Workshop).

R. F. Hampson
 June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Temp. Range/K | Reaction Rate Constant $k/cm^3 \text{ molecule}^{-1} s^{-1}$ | Uncert. Factor at 298K, notes |
|-------|----------------------------------|------------------|--|----------------------------------|
| 1.21 | $O + H_2 \rightarrow HO + H$ (2) | | ΔH (298) = 8 kJ/mol | |
| 10.19 | $H + HO \rightarrow O + H_2$ (2) | | | |
| | Dubinsky, McKenney (1975) | 350-230 | $k_f = 1.6 \times 10^{-11} \exp(-4570/T)$ | 1.5 (a) |
| | Baulch, et al (1972) review | 400-2000 | $k_f = 3.0 \times 10^{-14} (T) \exp(-4480/T)$ | |
| | Schott, et al (1974) | 1400-1900 | $k_r = k_f/K_{eq} = 1.4 \times 10^{-14} (T) \exp(-3500/T)$ | |
| | Campbell, Handy (1975) | 363-490 | $k_f/k_{ref} = 3.6 \pm 0.7$ Ref rxn is $O_2 + H \rightarrow O + HO$ | |
| | | | $k_f = 5.1 \times 10^{-11} \exp(-4950/T)$ | |
| | | | (a) Authors' recommended expression based on all low temperature data | |

This evaluation accepts the recommendation of Dubinsky and McKenney (1975) for k_f over this temperature range. For k_f at higher temperatures and for k_r use the recommended expressions in Baulch, et al (1972)

REFERENCES

- Baulch, D. L., Drysdale, D. D., Horne, D. G., and Lloyd, A. G., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 1: Homogeneous Gas Phase Reactions of the H_2 - O_2 System," (Butterworths, London, 1972)
- Campbell, I. M., and Handy, R. J., "Studies of Reactions of Atoms in a Discharge Flow Stirred Reactor Part I - The $O + H_2 \rightarrow HO$ System," J. Chem. Soc., Faraday Trans. 1 **71**, 2097-2106 (1975)
- Dubinsky, R. M., McKenney, D. J., "Determination of the Rate Constant of the $O + H_2 \rightarrow OH + H$ Reaction using Atomic Oxygen Resonance Fluorescence and the Air Afterglow Techniques," Can. J. Chem. **55**, 3531-3541 (1975)
- Schott, G. L., Getzinger, R. W., and Seitz, W. A., "Transient Oxygen Atom Yields in H_2O_2 Ignition and the Rate Coefficient for $O + H_2 \rightarrow OH + H$," Int. J. Chem. Kinet. **8**, 921-943 (1974)

R. F. Hampson
May 1978

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

This expression is that of Davis et al (1974). In view of the difficulties in studying H_2O_2 reactions, another study is needed to confirm the rate constant, especially at low temperatures. A-factor seems low

REPERBANC

- Albers, E. A., Hoyermann, E., Wagner, E. Gg., and Waltrum J., "Absolute Measurements of Rate Coefficients for the Reactions of H and O Atoms with H_2O_2 and H_2O ," Sympo Combust, 13th (Combustion Institute, Pittsburgh, 1971) 81-88
- CODATA(1979)k Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.
- Davis, D. D., Wong, W., and Schiff, E., "A Dye Laser Flash Photolysis Kinetics Study of the Reaction of Ground-State Atomic Oxygen with Hydrogen Peroxide," J. Phys. Chem. **12**, 463-464 (1974)
- Foner, S. N., and Hudson, E. L., "Mass Spectrometry of the HO_2 Free Radical," J. Chem. Phys. **36**, 2681-2689 (1962)
- NASA (1979), Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," E. D. Hudson and E. L. Reed, Editors, Deco 1979 (report of the June 1979 Harpers Ferry Workshop).

Dr. F. Hanson
June 1979

CHEMICAL KINETICS DATA SURVEY
 PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Temp. Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncertainty Factor at 298K, notes |
|------|--|------------------|--|--------------------------------------|
| 1.25 | O + HNO ₂ → H ₂ O + NO ₂ Kaiser, Japar (1978a) | 300 | ΔH (298) = - 57 kJ/mol 1 × 10 ⁻¹⁵ | |

Note that this is an upper limit only

REFERENCES

Kaiser, E. W., and Japar, S. W., "Upper Limits to the Gas Phase
 Reaction Rates of HONO with NH₃ and O(³P) Atoms"
 J. Phys. Chem. 82, 2753-2754 (1978a)

E. W. Hampson
 May 1978

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No | Reaction/Reference | Temp Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncert Factor at 298K, notes |
|------|--|-----------------|--|---------------------------------|
| | | | | |
| 1.26 | O + NO ₂ → NO + NO ₂ | | ΔH (298) = - 4 kJ/mol | |
| | NASA (1979) eval | 298 | < 3 x 10 ⁻¹⁷ | |
| | Chapman, Wayne (1974) | 300 | < 3 x 10 ⁻¹⁷ | |
| | Hampson, et al (1973) review | 300 | < 1.5 x 10 ⁻¹⁴ | |
| | Morley, Smith (1972) | 300 | < 1.3 x 10 ⁻¹⁴ | |

This recommendation accepts the upper limit reported by Chapman and Wayne (1974)

REFERENCES

- Chapman, C. J., and Wayne, R. P., "The Reaction of Atomic Oxygen and Hydrogen with Nitric Acid," *Int. J. Chem. Kinet.* **6**, 617-630 (1974)
- Hampson, R. P., (editor), "Survey of Photochemical and Rate Data for Twenty-Eight Reactions of Interest in Atmospheric Chemistry," *J. Phys. Chem. Ref. Data* **2**, No. 2 pgs. 267-312 (1973). These are revised versions of data sheets originally distributed as NBS Reports 10692 and 10828.
- Morley, C., and Smith, I. W. M., "Rate Measurements of Reactions of OH by Resonance Absorption, Part I. Reactions of OH with NO₂ and NO," *J. Chem. Soc., Faraday Trans. II* **68**, 1016-1030 (1972)
- NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," R. D. Hudson and R. I. Reed, Editors, Deco 1979 (report of the June 1979 Harpers Ferry Workshop).

R. P. Hampson
 June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Temp. Range/K | Reaction Rate Constant $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | Uncert. Factor at 298K, notes |
|-------|---|------------------|--|----------------------------------|
| 1.26a | O + H ₂ MO ₂ → products NASA (1979) eval | 298 | 1×10^{-15} | 5 |

Preliminary value of Trevor, Chang, Barker and Chang.

REFERENCES

- NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," E. D. Hudson and E. L. Reed, Editors, Dec. 1979 (report of the June 1979 Harpers Ferry Workshop).
- Trevor, Chang, Barker and Chang, private communication (1979).
- E. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Uncertainty Factor
 at 298K, notes

| No. | Reaction/Reference | Temp. Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncertainty Factor at 298K, notes |
|------|---|------------------|--|--------------------------------------|
| 1.27 | C + SO ₂ → SO ₂ + hv Baulch, et al (1976) review | | ΔH (298) = -550 kJ/mol no recommendation | |

See the review of Baulch, et al (1976) for a discussion of reported results. However, because of an insufficient data base, no recommendation can be made.

REFERENCES

Baulch, D. L., Drysdale, D. D., Duxbury, J., and Grant, S. J., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 3: Homogeneous Gas Phase Reactions of the C₂-C₃ System, the C₆-C₂-H₂ System, and of Sulphur-Containing Species," (Butterworths, London, 1976)

R. F. Hampson
 May 1978

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Temp. Range/K | Reaction Rate Constant $k/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$ | Uncert. Factor at 298K, notes |
|-------|--|------------------|---|----------------------------------|
| 1.27M | $\text{O} + \text{SO} \rightarrow \text{M} + \text{SO}_2 \rightarrow \text{M} \quad (1)$ | | $\Delta H (298) = -550 \text{ kJ/mol}$ | |
| 28. M | $\text{SO}_2 + \text{M} \rightarrow \text{O} + \text{SO} \rightarrow \text{M} \quad (2)$ | | | |
| | Baulch, et al (1976) review | 298 | $k_2 = 1.9 \times 10^{-31} \text{ cm}^6\text{molecule}^{-2}\text{s}^{-1}$ M = Ar k_2 no recommendation | 1.3 |
| | Schofield (1973) review | 300 | $k_2 = 8.8 \times 10^{-31}$ M = Ar | |
| | | 4500-7500 | $k_2 = 4.2 \times 10^{-10} \exp(-55000/T)$ | |

This evaluation accepts the recommendations in the review of Baulch, et al (1976)

REFERENCES

- Baulch, D. L., Drysdale, D. D., Duxbury, J., and Grant, S. J., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 3: Homogeneous Gas Phase Reactions of the C_2 - C_3 System, the C_4 - C_2 - H_2 System, and of Sulphur-Containing Species," (Butterworths, London, 1976)
- Schofield, K., "Evaluated Chemical Kinetic Rate Constants for Various Gas Phase Reactions," J. Phys. Chem. Ref. Data 2, 25-84 (1973)
- P. F. Hampson
May 1978

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No | Reaction/Reference | Temp. Range/K | Reaction Rate Constant k/cm ⁶ molecule ⁻² s ⁻¹ | Uncert Factor at 298K, notes |
|-------|---|------------------|--|---------------------------------|
| 1.28M | $C + SO_2 \rightarrow M \rightarrow SO_3 \cdot M$ CODATA (1979) eval | 200-400 | $\Delta H(298) = -348 \text{ kJ/mol}$ $k = 4.0 \times 10^{-32} \exp(-1000/T)$, $M = N_2$ no recommendation for k_{∞} | 2 |
| | Davis (1976) | 220-352 | $3.4 \times 10^{-32} \exp(-1130/T)$, $M = N_2$ $N_2(1.0)$, He(c.45), Ar(c.87), $SO_2(56)$ | |
| | Schofield (1973) review | 250-1000 | $1 \times 10^{-33} \exp(+500/T)$ $M = O_2, N_2, Ar, He$ | |
| | Atkinson, Pitts (1974) | 299-392 | $9.2 \times 10^{-32} \exp(-1000/T)$, $M = N_2^d$ | |
| | Ventersberg, deHaas (1975d) | 248-415 | $1.07 \times 10^{-31} \exp(-1400/T)$, $M = He$ Ref: eff: He(1.0), $N_2(2.4)$, $SO_2(.95)$ no recommendation | |
| | Baulch, et al (1976) review | | | |

Baich, D. L., Drysdale, D. D., Durbury, J., and Grant, S. J., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 3: Homogeneous Gas Phase Reactions of the C_2 - C_3 System, the C_6 - C_2 - H_2 System, and of Sulphur-Containing Species," (Butterworths, London, 1976)

CDATA(1979). Recommendations of the CDATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.

Davis, D. D., "Absolute Rate Constants for Elementary Reactions of Atmospheric Importance: Results from the University of Maryland Gas Kinetics Laboratory," Report 3 (Univ. of Maryland, College Park, Md. 20742, 1976)

Schozfeld, E. "Evaluated Chemical Kinetic Rate Constants for Various Gas Phase Reactions," *J. Phys. Chem. Ref. Data* **2**, 25-84 (1973)

Ventersberger, A. A., and deHeen, N. "Rate of the Reaction of $\text{O} + \text{SO}_2 + \text{N}_2$ - $\text{SO}_3 + \text{N}_2$." J. Chem. Phys. 63, 5411-5415 (1975d)

Mc P. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Uncertain Factor
at 298K, notes

| Reaction/Reference | Temp. Range/K | Reaction Rate Constant $k/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$ | Uncertain Factor at 298K, notes |
|---|----------------------|--|------------------------------------|
| 1.29 O + SO ₂ → products Baulch, et al (1976) review Westenberg, deHaas (1975c) | 298-507 | no recommendation $1.4 \times 10^{-31} \exp(785/T) \text{ cm}^3\text{molecule}^{-2}\text{s}^{-1}$ Rel. eff: Re(1.0), N ₂ (1.4) (a) Reaction O + SO ₂ → M → products found to be 3rd order up to P = 7 Torr; SO ₂ not detected | (a) |
| Schofield (1973) review Jacob, Winkler (1972) | 1480-1550 300-500 | $5 \times 10^{-10} \exp(-6000/T)$ $3 \times 10^{-16} \exp(-500/T)$ | uncertain |

See the review of Baulch, et al (1976) for a discussion of reported results. However, because of total lack of agreement of all studies, no recommendation can be made

REFERENCES

- Baulch, D. L., Drysdale, D. D., Duxbury, J., and Grant, S. J., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 3: Homogeneous Gas Phase Reactions of the O₂-O₃ System, the CO-O₂-H₂ System, and of Sulphur-Containing Species," (Butterworths, London, 1976)
- Jacob, A., and Winkler, C. A., "Kinetics of the Reactions of Oxygen Atoms and Nitrogen Atoms with Sulphur Trioxide," J. Chem. Soc., Faraday Trans. 1 **68**, 2077-2082 (1972)
- Schofield, K., "Evaluated Chemical Kinetic Rate Constants for Various Gas Phase Reactions," J. Phys. Chem. Ref. Data **2**, 25-84 (1973)
- Westenberg, A. A., and deHaas, N., "Rate of the O + SO₂ Reaction," J. Chem. Phys. **42**, 725-730 (1975c)
- B. F. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTES, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Tempo Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncerto. Factor at 298K, notes | |
|------|---|------------------|--|-----------------------------------|---|
| | | | | | |
| 1.31 | O + HS → H + SO Cupitt, Glass (1975) Baulch, et al (1976) | 295 | ΔH (298) = -172 kJ/mol 1.6 ± 0.5 × 10 ⁻¹⁰ no recommendation | | 2 |

This evaluation accepts the result of Cupitt and Glass with increased error limits. See the review of Baulch, et al (1976) for a discussion of reported results

REFERENCES

- Baulch, D. L., Drysdale, D. D., Duxbury, J., and Grant, S. J., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 3: Homogeneous Gas Phase Reactions of the O₂-O₃ System, the C6-D₂-H₂ System, and of Sulphur-Containing Species," (Butterworths, London, 1976)
- Cupitt, L. T., and Glass, G. P., "Reactions of SH with Atomic Oxygen and Hydrogen," *Int. J. Chem. Kinet.*, Symp. No. 1, 39-50 (1975)
- P. F. Hampson
May 1978

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Tempo Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncerto. Factor at 298K, notes |
|------|---|--|--|-----------------------------------|
| 1,32 | $O + H_2S \rightarrow H_2O + HS$ NASA (1979) eval COPDATA (1979) eval Singleton, et al (1979) Siegler, et al (1978) Whytock, et al (1976) Hollinden, Kurylo, Timmons (1970) | 200-300 250-500 297-502 281-497 263-495 205-300 | $\Delta H (298) = -44 \text{ kJ/mol}$ $2.6 \times 10^{-11} \exp(-(2170 \pm 750)/T)$ $7.2 \times 10^{-12} \exp(-(1660 \pm 150)/T)$ $2.6 \times 10^{-11} \exp(-2170/T)$ $k(301 \text{ K}) = 3.6 \times 10^{-14}$ $7.24 \times 10^{-12} \exp(-1660/T)$ $2.9 \times 10^{-13} \exp(-750/T)$ (a) Assumes stoichiometry of 3,5 | 2 1.3 (a) |

This recommendation accepts the recent determination by Singleton et al (1979). The uncertainty factor in $k(298)$ was chosen to encompass the values of $k(298)$ determined by Hollinden et al (1970), Whytock et al (1976) and Slagle et al (1978). The E/R value is that of the Singleton study as confirmed by the higher temperature data of Whytock et al and the measurements of Slagle et al. It should be emphasized that the Singleton determination did not extend below 298K. The only existing data below 298K appear to indicate a dramatic change in E/R in this temperature region. Thus $\Delta E/R$ was set to account for these observations. Such a nonlinearity in the Arrhenius plot might indicate a change in reaction mechanism from abstraction (as written) to addition. An addition channel has been proposed for $\text{O} + \text{H}_2\text{S}$ by Slagle et al (1978) as well as Singleton, and addition products from this reaction have been seen in a matrix. (Smardzewski and Lin (1977)). Further kinetic study is recommended in the 200 to 300K range. Direct mechanistic information is needed

REFERENCES

CCDATA(1979). Recommendations of the CCData Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.

Hollinden, G. A., Kurylo, M. J., and Timmons, R. B., "Electron Spin Resonance Study of the Kinetics of the Reaction of $\text{C}(^3\text{P})$ Atoms with N_2 ," *J. Phys. Chem.* **74**, 588-591 (1970)

NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," R. D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the June 1979 Harpers Ferry Workshop).

Singleton, C. L., Irwin, R. S., Nip, W. S., and Cvjetanović, R. J.,
"Kinetics and Mechanism of the Reaction of Oxygen Atoms with
Hydrogen sulfide," J. Phys. Chem. B, 215-220 (1979)

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Tempo Range/K | Reaction Rate Constant $k/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$ | Uncert. Factor at 298K, notes |
|-------|---|------------------|--|----------------------------------|
| 1,34a | $\text{F} + \text{CS} \rightarrow \text{CF} + \text{S}$ | | $\Delta H(298) = -355 \text{ kJ/mol}$ | |
| | CNATA (1979) eval | 150-300 | $2.7 \times 10^{-10} \exp(-(760 \pm 250)/T)$ | 1.25 |
| | Littenfeld, Richardson (1977) | 150-300 | $2.6 \times 10^{-10} \exp(-760/T)$ | |
| | Baulch, et al (1976) review | 300 | 2.2×10^{-11} | |
| | Bide, et al (1976) | 300 | 2.24×10^{-11} | |
| | Slagle, et al (1975) | 305 | 2.06×10^{-11} | |

Recommendation accepts the temperature dependence of Lilenfeld and Richardson (1977) and averages the room temperature values from this and other recent studies

REFERENCES

- Baulch, D. L., Drysdale, D. D., Duxbury, J., and Grant, S. J., "Evaluated Kinetic Data for High Temperature Reactions", Vol. 3: Homogeneous Gas Phase Reactions of the O₂-C₃ System, the C₂H₂-H₂ System, and Gas Sulphur-Containing Species," (Butterworths, London, 1976)
- Bide, C. T., Breckenridge, W. H., and Kohn, W. S., "A Kinetic Study of the Very Fast Reaction: $\text{C}(\text{^3P}) + \text{CS} \rightarrow \text{CS}^+ + \text{S}(\text{^3P})$," J. Chem. Phys. **54**, 3296-3302 (1976)
- CFDATA(1975)6 Recommendations of the CFDATA Task Group on Chemical Kinetics, To be published in the Journal of Physical and Chemical Reference Data
- Gillenfeld, H. V., and Richardson, R. J., "Temperature Dependence of the Rate Constant for the Reaction between Carbon Monosulfide and Atomic Oxygen," J. Chem. Phys. **67**, 3991-3997 (1977)
- Slagle, J. P., Graham, R. E., Gilbert, J. R., and Gutman, D., "Direct Determination of the Rate Constant for the Reaction of Oxygen Atoms with Carbon Monosulfide," Chem. Phys. Lett. **32**, 189-186 (1975)

Rc Fc Hampson
June 197c

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Temp. Range/K | Reaction Rate Constant $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | Uncert. Factor at 298K, notes |
|-------|--|---|---|----------------------------------|
| 1.34b | $\text{O} + \text{CS}_2 \rightarrow \text{CS} + \text{S}_2$ (a) $\rightarrow \text{COS} + \text{S}$ (b) NASA (1979) eval CODATA (1979) eval Baulch, et al (1976) review Wei, Timmons (1975) Stagle, Gilbert, Gutman (1974) Graham, Gutman (1977) Westenberg, deHaas (1969) Callear, Hedges (1970) Callear, Smith (1967) Hosmann, et al (1968) | 200-300 200-500 200-1000 218-293 302 249-500 227-538 298 305 300-920 | $\Delta H(298) = -89 \text{ kJ/mol}$ $= -231 \text{ kJ/mol}$ $k_a = 3.1 \times 10^{-11} \exp(-(640 \pm 150)/T)$ $k = 5.8 \times 10^{-11} \exp(-(700 \pm 100)/T)$ $k_a = 3.7 \times 10^{-11} \exp(-700/T)$ $k = 2.8 \times 10^{-11} \exp(-640/T)$ $k = 4.0 \times 10^{-12}$ $k_b/k = 0.093$ k_p/k decreases from 0.098 at 249K to 0.081 at 500K. Overall rate also reported. $2.0 \times 10^{-11} \exp(-530/T)$ 3.7×10^{-12} 4.2×10^{-12} $8.3 \times 10^{-12} \exp(-950/T)$ | 1.12 1.5 |

The value of $k(298 \text{ K})$ is the average of six determinations: Wei and Timmons (1975), Westenberg and deHaas (1969), Stagle et al (1974), Callear and Smith (1967), Callear and Hedges (1970) and Hosmann et al (1968). The E/R value is that of Wei and Timmons (1975). A E/R has been set to encompass within a 2 σ error band the limited temperature data of Westenberg and deHaas (1969)

REFERENCES

- Baulch, D. L., Drysdale, D. D., Duxbury, J., and Grant, S. J., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 3: Homogeneous Gas Phase Reactions of the O_2 - O_3 System, the $\text{C}_6\text{-C}_2\text{-H}_2$ System, and of Sulphur-Containing Species," (Butterworths, London, 1976)
- Callear, A. B., and Hedges, R. E. M., "Flash Spectroscopy with Mercury Resonance Radiation. Part 1. An Experimental Method with Microwave-pulse Excitation," Trans. Faraday Soc. **66**, 605-614 (1970)
- Callear, A. B., and Smith, I. W. M., "Measurement of the Rate Parameters for Reaction of $\text{O}(^2\text{P})$ with Carbon Disulphide and Chlorine, by Flash Spectroscopy," Nature **213**, 382-383 (1967)

CODATA (1979). Recommendations of the CODATA Task Group on Chemical

Kinetics. To be published in the Journal of Physical and Chemical
Reference Data.

- Graham, R. E., and Gutman, D., "Temperature Dependence of Rate
Constants and Branching Ratios for the Reaction of Oxygen
Atoms with Carbon Disulfide," *J. Phys. Chem.* **81**, 207-209 (1977)
- Rosen, L. B., Krome, G., and Wagner, R. G., "Schwefelkohlenstoff-
oxydation, Geschwindigkeit von Elementarreaktionen. Teil I,"
Ber. Bunsenges. Phys. Chem. **72**, 998-1004 (1968)
- NASA (1979). Recommendations of the NASA Panel for Data Evaluation,
published in NASA SP 1046 "The Stratosphere: Present and Future,"
B. D. Hudson and F. L. Reid, Editors, Dec. 1979 (report of the
June 1979 Warner Ferry Workshop)
- Slagle, I. R., Gilbert, R. W., and Gorman, D., "Kinetics of the Reaction
between Oxygen Atoms and Carbon Disulfide," *J. Chem. Phys.* **81**,
764-765 (1979)
- Seaton, A. G., and Doherty, N., "Atom-Molecule Kinetics
Using SSB Detection. 1. Results for $C + OCS$, $C + CS_2$,
 $C + CO_2$, and $C + C_2H_4$," *J. Chem. Phys.* **50**, 707-719 (1969)
- R. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY

Uncert. Factor
at 298K, notes

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS
Reaction Rate Constant
k/cm³molecule⁻¹s⁻¹

| Reaction/Reference | Temp. Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncert. Factor at 298K, notes |
|-----------------------------|------------------|--|----------------------------------|
| 1.34c | 200-300 | 2.1 x 10 ⁻¹¹ exp(-213 kJ/mol) | 1.12 |
| 0 + OCS → SO + CO | 220-600 | 2.6 x 10 ⁻¹¹ exp(-2250±150)/T) | 1.5 |
| NASA (1979) eval | 296 | (1.39±0.14) x 10 ⁻¹⁴ | |
| CODATA (1979) eval | 239-404 | 2.0 x 10 ⁻¹¹ exp(-2150/T) | |
| Wannink, et al (1976) | 263-502 | 1.65 x 10 ⁻¹¹ exp(-2165/T) | |
| Wel, Timmons (1975) | 190-1200 | 2.6 x 10 ⁻¹¹ exp(-2250/T) | |
| Wel, Timmons (1974) | 297 | 1.19 x 10 ⁻¹⁴ | |
| Klemm, Stief (1976) review | 273-808 | 3.2 x 10 ⁻¹¹ exp(-2280/T) | |
| Baulch, et al (1976) review | | | |
| Brackenridge, Miller (1972) | | | |
| Wentenberd, deHaas (1969) | | | |

The value for k(298 K) is the average of five different studies of this reaction: Wentenberg and deHaas (1969), Klemm and Stief (1974), Wel and Timmons (1975), Manning et al (1976) and Brackenridge and Miller (1972). The recommended value for E/R is the average of those determined in the temperature studies reported in the first three references

REFERENCES

- Baulch, D. L., Drysdale, D. D., Duxbury, J., and Grant, S. J., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 3: Homogeneous Gas Phase Reactions of the O₂-O₃ System, the CO-O₂-H₂ System, and Gas Phase Reactions of the C₂-O₃ System," (Butterworths, London, 1976)
- Brackenridge, W. R., and Miller, T. A., "Kinetic Study by EPR of the Production and Decay of SO(1Δ) in the Reaction of O₂(1Δ_g) with SO(3Σ⁻)," J. Chem Phys. **56**, 465-474 (1972)
- CODATA(1979). Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Kinetics.

Reference Data.

- Klemm, R. E., and Stief, L. J., "Absolute Rate Parameters for the Reaction of Ground State Atomic Oxygen with Carbonyl Sulfide," *J. Chem. Phys.* **51**, 4900-4906 (1974)
- Manning, P. C., Braun, W., and Kurylo, M. J., "The Effect of Infrared Laser Excitation on Reaction Dynamics: $\text{O} + \text{C}_2\text{H}_4$ and $\text{O} + \text{OCS}$," *J. Chem. Phys.* **65**, 2609-2615 (1976)
- NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," R. D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the June 1979 Harpers Ferry Workshop).
- Vel, C. M., and Timmons, R. E., "ESR Study of the Kinetics of the Reactions of $\text{O}(^1\text{P})$ Atoms with CS_2 and OCS ," *J. Chem. Phys.* **62**, 3240-3245 (1975)
- Westenberg, A. A., and deHaas, M., "Atom-Molecule Kinetics using ESR Detection. V. Results for $\text{O} + \text{OCS}$, $\text{O} + \text{CS}_2$, $\text{O} + \text{NO}_2$, and $\text{H} + \text{C}_2\text{H}_4$," *J. Chem. Phys.* **50**, 707-719 (1969)
- R. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Temp. Range/K | Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$ | Uncertainty Factor at 298K, notes |
|------|--------------------------------|------------------|---|--------------------------------------|
| 1.36 | $O + ClO \rightarrow Cl + O_2$ | | $\Delta H (298) = -230 \text{ kJ/mol}$ | |
| | NASA (1979) eval | 200-300 | $7.7 \times 10^{-11} \exp(-(130 \pm 130)/T)$ | 1e2 |
| | CODATA (1979) eval | 220-425 | $7.5 \times 10^{-11} \exp(-(120 \pm 120)/T)$ | 1e25 |
| | Clyne, Nip (1976) | 220-426 | $1.07 \times 10^{-10} \exp(-224/T)$ | (a) |
| | | | (a) Selected by Watson (1977) review | |
| | Zahniser, Kaufman (1977) | 218-295 | $k/k_{ref} = (1.55 \pm 0.17) \exp(246 \pm 30/T)$ | (b) |
| | | | (b) $k_{ref} = k(Cl + O_3)$ | |
| | Bemand, et al (1973) | 298 | 5.3×10^{-11} | |

Unchanged from NASA 1010. The preferred values were derived in the same manner as the previous NASA evaluations. This expression is based on values of $5.0 \times 10^{-11} cm^3 molecule^{-1} s^{-1}$ and $4.4 \times 10^{-11} cm^3 molecule^{-1} s^{-1}$ at 298 and 230K, respectively. These values were deduced from the experimental data of Bemand et al (1973), Clyne and Nip (1976), and Zahniser and Kaufman (1977). The E/R values reported by Clyne and Nip and Zahniser and Kaufman are in poor agreement. Before this reaction can be considered to be well understood, additional data are required.

REFERENCES

- Bemand, P. P., Clyne, M. A., and Watson, W. T., "Reactions of Chlorine Oxide Radicals. Part 4.-Rate Constants for the Reaction $Cl + OClO$, $O + OClO$, $H + OClO$, $NO + OClO$ and $O + ClO$," *J. Chem. Soc. Faraday Trans. 1* **69**, 1356-1374 (1973)
- Clyne, M. A., and Nip, W. S., "Reactions of Chlorine Oxide Radicals. Part 6.-The Reaction $O + ClO \rightarrow Cl + O_2$ from 220 to 426 K," *J. Chem. Soc., Faraday Trans. 1* **72**, 2211-2217 (1976)
- CODATA(1979). Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.
- NASA RP-1010. "Chlorofluoromethanes and the Stratosphere" W. D. Hudson, Editor, August 1977 This reference contains the NASA (1977) rate constant recommendations.
- NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," W. D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the June 1979 Barbers Ferry Workshop).

Bates, R. L., "Rate Constants for Reactions of ClO_2 of Atmospheric Interest," J. Phys. Chem. Ref. Data **6**, 871-918 (1977)
Zahniser, M. S., and Kaufman, F., "Kinetics of the Reactions of ClO with O and with NO ," J. Chem. Phys. **66**, 3673-3681 (1977)

R. F. Hansen
June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Temp. Range/K | Reaction Rate Constant $k/\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ | Uncertainty Factor at 298K, notes |
|--------|--|------------------|--|--------------------------------------|
| 1,36Br | $\text{O} + \text{BrO} \rightarrow \text{Br} + \text{O}_2$ | | $\Delta H(298) = -263 \text{ kJ/mol}$ | |
| | NASA (1979) eval | 200-300 | $3 \times 10^{-11} \exp((0 \pm 250)/T)$ | 3 |
| | CODATA (1979) eval | 298 | 3×10^{-11} | 3 |
| | Clyne, et al (1976) | 298 | 2.5×10^{-11} | |

Unchanged from NASA 1010. The preferred value is based on the value reported by Clyne et al (1976). This value appears to be quite reasonable in light of the known reactivity of ClO radicals with atomic oxygen. The temperature dependence of k is expected to be small for such an atom-radical process, e.g., $\text{O} + \text{ClO}$

REFERENCES

- Clyne, M. A. A., Monkhouse, P. B., and Townsend, L. W., "Reactions of O^3P_j Atoms with Halogens: The Rate Constants for the Elementary Reactions $\text{O} + \text{BrCl}$, $\text{O} + \text{Br}_2$, and $\text{O} + \text{Cl}_2$," *Int. J. Chem. Kinet.* **8**, 425-445 (1976)
- CODATA(1979). Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the *Journal of Physical and Chemical Reference Data*.
- NASA RP-1010. "Chlorofluoromethanes and the Stratosphere"
R. D. Hudson, Editor, August 1977 This reference contains the NASA (1977) rate constant recommendations.
- NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future,"
R. D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the June 1979 Harpers Ferry Workshop).

R. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Uncert. Factor
at 298K, notes

Reaction Rate Constant
k/cm³molecule⁻¹s⁻¹

Temp.
Range/K

Reaction/Reference

No.

| | | | | |
|-------|--|--|---------|---|
| 1.36F | $\text{O} + \text{F}_2 \rightarrow \text{F} + \text{OF}_2$ | $\Delta H (298) = -279 \text{ kJ/mol}$ | | |
| | NASA (1979) eval | $5 \times 10^{-11} \exp((0.4250)/T)$ | 200-300 | 3 |
| | CGATA (1979) eval | 5×10^{-11} | 298 | 3 |

New entry. This estimate is probably accurate to within a factor of 3, and is based upon the assumption that the reactivity of F_2 is similar to that of Cl_2 and Br_2 . The experimentally determined rate constants for Cl_2 and Br_2 at -298 K are $(5.2 \times 10^{-11} \text{ Watson (1977)})$ and $(2.5 \times 10^{-11} \text{ Clyne et al (1976)})$, respectively. The temperature dependence of the rate constant is expected to be small. The temperature dependence of the analogous Cl_2 reaction has been studied twice with somewhat different results. The values reported for H/H are -76 K Zahniser and Kaufman (1977) and $+224 \text{ K}$ Clyne and Nip (1976).

REFERENCES

Clyne, M. A. A., Monkhouse, P. B., and Townsend, L. W., "Reactions of O^3P Atoms with Halogens: The Rate Constants for the Elementary Reactions $\text{O} + \text{BrCl}$, $\text{O} + \text{Br}_2$, and $\text{O} + \text{Cl}_2$," *Int. J. Chem. Kinet.* **8**, 425-445 (1976)

Clyne, M. A. A., and Nip, W. S., "Reactions of Chlorine Oxide Radicals. Part 6.-The Reaction $\text{O} + \text{ClO} \rightarrow \text{Cl} + \text{O}_2$ from 220 to 426 K," *J. Chem. Soc., Faraday Trans. I* **72**, 2211-2217 (1976)

CGATA(1979). Recommendations of the CGATA Task Group on Chemical Kinetics. To be published in the *Journal of Physical and Chemical Reference Data*.

NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA EP 1049 "The Stratosphere: Present and Future," E. D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the June 1979 Harpers Ferry Workshop).

Watson, M. L., "Rate Constants for Reactions of ClO_2 of Atmospheric Interest," *J. Phys. Chem. Ref. Data* **6**, 871-918 (1977)

Zahniser, M. S., and Kaufman, F., "Kinetics of the Reactions of ClO with O and with NO ," *J. Chem. Phys.* **65**, 3673-3681 (1977)

E. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Temp. Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncert. Factor at 298K, notes |
|------|---|------------------|---|----------------------------------|
| 1.37 | O + OClO → ClO + O ₂ NASA (1979) eval Bemand, et al (1973) | 200-300 298 | ΔH (298) = -244 kJ/mol 2.5 × 10 ⁻¹¹ exp(-(1166±300)/T) 5 × 10 ⁻¹³ | 1.5 |

Minor modification from NASA 1010. Arrhenius expression was estimated based on 298 K data reported by Bemand, Clyne and Watson (1973)

REFERENCES

Bemand, P. P., Clyne, M. A. and Watson, R. T., "Reactions of Chlorine Oxide Radicals. Part 4.-Rate Constants for the Reaction Cl + OClO, O + OClO, H + OClO, NO + OClO and O + ClO," J. Chem. Soc., Faraday Trans. I 69, 1356-1374 (1973)

NASA RP-1010, "Chlorofluoromethanes and the Stratosphere"

R. D. Hudson, Editor, August 1977 This reference contains the NASA (1977) rate constant recommendations.

NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future,"

R. D. Hudson and E. L. Reed, Editors, Dec. 1979 (report of the June 1979 Harpers Ferry Workshop).

to P. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Temp. Range/K | Reaction Rate Constant $k/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$ | Uncert. Factor at 298K, notes |
|-------|---|------------------|--|----------------------------------|
| 1.37F | $\text{O} + \text{H}_2 \rightarrow \text{H} + \text{O}_2$ | | | |
| | NASA (1979) eval | 200-300 | 5×10^{-11} | 5 |
| | CODATA (1979) eval | 298 | 5×10^{-11} | 5 |

$\Delta H(298) = -153 \text{ kJ/mol}$
 $\exp((0.8250)T)$

New entry. No experimental data. The rate constant for such a radical-atom process is expected to approach the gas collision frequency, and is not expected to exhibit a strong temperature dependence

REFERENCES

CODATA(1979). Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.

NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA SP 1049 "The Stratosphere: Present and Future," E. D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the June 1975 Harpers Ferry Workshop).

E. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Temp. Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncerto Factor at 298K, notes |
|------|----------------------------|------------------|--|----------------------------------|
| 1,39 | O + HCl → HO + Cl | | ΔH (298) = 3 kJ/mol | |
| | NASA (1979) eval | 200-300 | 1.14 x 10 ⁻¹¹ exp(-3370±350)/T) | 2 |
| | CODATA (1979) eval | 293-718 | 1.1 x 10 ⁻¹¹ exp(-3370±350)/T) | 2 |
| | Bavishankara, et al (1977) | 350-454 | 5.2 x 10 ⁻¹¹ exp(-3755/T) | |
| | Hack, et al (1977) | 293-718 | 8.5 x 10 ⁻¹² exp(-3220/T) | |
| | Brown, Smith (1975) | 293-440 | 2.5 x 10 ⁻¹² exp(-2970 ± 150/T) | |
| | Wong, Ballem (1972) | 356-628 | 1.5 ± 0.3 x 10 ⁻¹¹ exp (-3580/T) | |
| | Balakbhin. et al (1971) | 295-371 | 1.74 ± 0.6 x 10 ⁻¹² exp(-2260/T) | |

Unchanged from NASA 1010. Fair agreement exists between the results of Brown and Smith (1975), Wong and Belles (1971), Bavishankara et al (1977a) and Hack et al (1977) at 300 K (some of the values quoted for k (300 K) were obtained by extrapolation of the experimentally determined Arrhenius expressions), but these are a factor of ~ 7 lower than that of Balakhnin et al (1971). Unfortunately the values reported for E/R are in complete disagreement, ranging from 2260-3755 K. The preferred value was based on the results reported by Brown and Smith, Wong and Belles, Bavishankara et al, and Hack et al but not those reported by Balakhnin et al

REFERENCES

Balakhnin, V. P., Egorev, V. I., and Intezarova, E. I., "Kinetics Investigation of the Elementary Reactions of Oxygen Atoms in the Gas Phase by EPR. II. The Reaction O + HCl → OH + Cl," Kinet. Catal. 12, 258-262 (1971);
 trs of: Kinet. Catal. 12, 299-303 (1971)

Brown, R. D. H., and Smith, I. W. M., "Absolute Rate Constants for the Reactions O(3P) Atoms with HCl and HBr," Int. J. Chem. Kinet. 7, 301-315 (1975)

CODATA(1979). Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.

- Reck, W., Mex. G., and Wagner, H. G., "Bestimmung der Geschwindigkeitskonstanten der Reaktionen $\text{O} + \text{HCl}$ im Temperaturbereich 293 bis 716 K und $\text{OH} + \text{HCl}$ bei 293 K," *Ber. bunsenges. Phys. Chem.* **81**, 677-694 (1977)
- NASA RP-1010, "Chlorofluoromethanes and the Stratosphere" R. D. Hudson, Editor, August 1977 This reference contains the NASA (1977) rate constant recommendations, NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," R. D. Hudson and E. L. Reed, Editors, Dec. 1979 (report of the June 1979 Harpers Ferry Workshop).
- Ravishankara, A. R., Smith, G., Watson, R. T., and Davis, D. D., "A Temperature Dependent Kinetics Study of the Reactions of HCl with OH and $\text{O}(^3\text{P})$," *J. Phys. Chem.* **81**, 2220-2225 (1977)
- Wong, E. L., and Belles, F. E., "Rate Measurements for the Reaction of Hydrogen Chloride and Deuterium Chloride with Atomic Oxygen," Lewis Research Center, NASA, Cleveland, Ohio, NASA Tech. Note, NASA TN-D-6495 (1971); *Chem. Abstr.* **76**:18326q (1972)
- R. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Tempo Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncerte. Factor at 298K, notes |
|------|--|------------------|--|-----------------------------------|
| 1.39 | $O + HCl(v=1) \rightarrow HO + Cl(a)$ $\rightarrow O + HCl(v=0)(b)$ *Brown, Glass, Smith (1975) Arnoldi, Wolfrum (1974) | 196-400 300 | $\Delta H(298) = -31 \text{ kJ/mol}$ $\quad \quad \quad = -34 \text{ kJ/mol}$ $6.2 \times 10^{-12} \exp(-530/T)$ $3.6 \pm 1.2 \times 10^{-12}$ (a) Total rate constant for sum of two reaction paths. | 3 (a) (a) |

This evaluation accepts the results of the temperature dependent study of Brown, Glass and Smith (1975), but with increased error limits because of the large discrepancy with the room temperature results of Arnoldi and Wolfrum (1974)

REFERENCES

- Arnoldi, D., and Wolfrum, J., "The Reaction of Vibrationally Excited HCl with Oxygen and Hydrogen Atoms," *Chem. Phys. Lett.* **24**, 234-238 (1974)
- Brown, R. D., Glass, G. F., and Smith, I. W. M., "The Relaxation of HCl(v=1) and DCl(v=1) by O Atoms Between 196 and 400 K," *Chem. Phys. Lett.* **32**, 517-520 (1975)
- E. F. Hampson
 May 1976

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Temp. Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncerto Factor at 298K, notes |
|--------|------------------------------|------------------|--|----------------------------------|
| 1.39Br | 0 + HBr -> H2 + Br | | $\Delta H(298) = -62 \text{ kJ/mol}$ | |
| | NASA (1979) eval | 200-300 | $7.6 \times 10^{-12} \exp(-(1571 \pm 300)/T)$ | 1.5 |
| | CODATA (1979) eval | 250-400 | $7.0 \times 10^{-12} \exp(-(1560 \pm 300)/T)$ | 1.5 |
| | Singleton, Cvitanovic (1978) | 258-554 | $1.34 \times 10^{-11} \exp(-1807/T)$ | |
| | Brown, Smith (1975) | 267-430 | $4.0 \times 10^{-12} \exp(-1360 \pm 50/T)$ | |
| | Takacs, Glass (1973c) | 258 | $(4.4 \pm 1.0) \times 10^{-14}$ | |

Unchanged from NASA 1010. As the values reported for k at 298 K (Takacs and Glass (1973c), Brown and Smith (1975) and Singleton and Cvitanovic (1978)) are in fair agreement, the mean is taken to be the preferred value. The agreement between the values deduced from the Arrhenius expressions reported in stratospheric temperatures is rather poor, e.g., the values differ by ~ 70% at 250K. The preferred value has been synthesized to best fit both sets of data between 250 and 400 K. The A-factor derived for the preferred expression and that reported by Brown and Smith appear to be lower than would be expected. This, combined with the absence of data at stratospheric temperature, leads to considerable uncertainty in the values of k between 200 and 260 K

REFERENCES

Brown, R. D. E., and Smith, I. W. M., "Absolute Rate Constants for the Reactions of (3p) Atoms with HCl and HBr," *Int. J. Chem. Kinet.* **7**, 301-315 (1975)

CODATA(1979). Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the *Journal of Physical and Chemical Reference Data*.

NASA RP-1010. "Chlorofluoromethanes and the Stratosphere" R. D. Hudson, Editor, August 1977 This reference contains

the NASA (1977) rate constant recommendations.
NASA (1979). Recommendations of the NASA Panel for Data Evaluation,
published in NASA RP 1049 "The Stratosphere: Present and Future,"
E. De Hudson and E. L. Reed, Editors, Dec. 1979 (report of the
June 1979 Harpers Ferry Workshop).
Singleton, D. L., and Cveticanovic, E. J., "Temperature
Dependence of Rate Constants for the Reactions of Oxygen
Atoms, O(³P), with N₂ and N₂O," Can. J. Chem. **56**,
2934-2939 (1978)
Takaue, G. A., and Glass, G. P., "Reaction of Atomic Oxygen with Hydrogen
Bromide," J. Phys. Chem. **77**, 1182-1186 (1973c)
R. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Temp. Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncert. Factor at 258K, notes |
|------|---|------------------|--|----------------------------------|
| 1.40 | O + NOCl → ON + ClO NASA (1979) eval | 200-300 | $\Delta H (298) = -30 \text{ kJ/mol}$ $1 \times 10^{-11} \exp(-(2200 \pm 800)/T)$ | 10 |

New entry. There are no experimental data; this is an estimated value based on rates of O-atom reactions with similar compounds

REFERENCES

NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," E. D. Hudson and E. L. Reed, Editors, Dec. 1979 (report of the June 1975 Harper's Ferry Workshop).

E. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Temp. Range/K | Reaction Rate Constant $k/\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ | Uncerto Factor at 298K, notes |
|-------|---|------------------|--|----------------------------------|
| | | | | |
| 1.43a | $\text{O} + \text{NO}_3\text{Cl} \rightarrow \text{products}$ | | | |
| | NASA (1979) eval | 200-300 | $3.0 \times 10^{-12} \exp(-8080/200/T)$ | 1.5 |
| | CDATA (1979) | 213-295 | $3.0 \times 10^{-12} \exp(-8080/200/T)$ | 1.25 |
| | Molina, et al (1977a) | 213-295 | $3.4 \times 10^{-12} \exp(-840/T)$ | |
| | Kurylo (1977) | 225-273 | $1.5 \times 10^{-12} \exp(-692/T)$ | |
| | Ravishankara, et al (1977) | 245 | 2×10^{-13} | |

Unchanged from NASA 1010. The results reported by Molina et al (1977a) and Kurylo (1977) are in good agreement, and this data has been used to derive the preferred Arrhenius expressions. The value reported by Ravishankara et al (1977) at 245 K is a factor of 2 greater than those from the other studies and this may possibly be attributed to (a) secondary kinetic complications, (b) presence of NO_2 as a reactive impurity in the ClONO_2 , or (c) formation of reactive photolytic products. None of the studies reported identification of the reaction products

REFERENCES

- CDATA(1979). Recommendations of the CDATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.
- Kurylo, M. J., "Flash Photolysis Resonance Fluorescence Investigation of the Reaction of $\text{O}(^3\text{P})$ Atoms with ClONO_2 ," Chem. Phys. Lett. **49**, 467-470 (1977)
- Molina, L. J., Spencer, J. E., and Molina, M. J., "The Rate Constant for the Reaction of $\text{O}(^3\text{P})$ Atoms with ClONO_2 ," Chem. Phys. Lett. **45**, 168-162 (1977a)
- NASA RP-1010. "Chlorofluoromethanes and the Stratosphere"

R. D. Hudson, Editor, August 1977 This reference contains the NASA (1977) rate constant recommendations, NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," R. D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the June 1979 Harpers Perry Workshop).

Davieshankar, A. R. Davis, D. D. Smith, G., Tesi, G., and Spencer, J., "A Study of the Chemical Degradation of ClONO_2 in the Stratosphere," *Geophys. Res. Lett.* 4, 7-9 (1977)

R. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Temp. Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncertainty Factor at 298K, notes |
|------|--|------------------|--|--------------------------------------|
| 1.44 | $O + Cl_2 \rightarrow ClO + Cl$ Clyne, et al (1976) | 174-602 | $\Delta H (298) = -26 \text{ kJ/mol}$ $4.2 \times 10^{-12} \exp(-1370/T)$ | 1.6 |

This recommended expression was derived by Clyne, et al [1976] on the basis of results in this study (299-602K) and other recent work. It is also recommended in the Watson (1977) review

REFERENCES

- Clyne, M. A., A. Monkhouse, P. B., and Townsend, L. W., "Reactions of $O(^3P)$ Atoms with Halogens: The Rate Constants for the Elementary Reactions $O + BrCl$, $O + Br_2$, and $O + Cl_2$," *Int. J. Chem. Kinet.* **8**, 425-445 (1976)
- Watson, R. T., "Rate Constants for Reactions of ClO_2 of Atmospheric Interest," *J. Phys. Chem. Ref. Data* **6**, 871-918 (1977)
- P. F. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Temp. Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncertainty Factor at 298K, notes |
|-------|--|------------------|--|--------------------------------------|
| 1.44a | C + Cl ₂ O → 2ClO Watson (1977) review | 300 | ΔH (298) = -126 kJ/mol 1.4 × 10 ⁻¹¹ | 1.5 |

This evaluation accepts the recommendation in the Watson (1977) review

REFERENCES

- Watson, R. T., "Rate Constants for Reactions of ClO₂ of Atmospheric Interest," J. Phys. Chem. Ref. Data 6, 971-918 (1977)
- R. F. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Temp. Range/K | Reaction Rate Constant $k/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$ | Uncert. Factor at 298K, notes |
|-------|--|------------------|--|------------------------------------|
| 1.45M | $\text{O} + \text{C}_2\text{H}_4 \rightarrow \text{M} + \text{C}_2\text{H}_2 + \text{M}$ (2) | | $\Delta H(298) = -532 \text{ kJ/mol}$ | |
| 46M | $\text{C}_2\text{H}_2 + \text{M} \rightarrow \text{O} + \text{C}_2\text{H}_4 + \text{M}$ (r) | | | |
| | Baulch, et al (1976) review | 250-500 | $k_f = 6.5 \times 10^{-33} \exp(-2180/T) \text{ cm}^6\text{molecule}^{-2}\text{s}^{-1}$ M = C ₂ H ₄ | 1.2 at 250K inc. to 2.0 at 500K |
| | | 296 | $k_f = 2.3 \times 10^{-36} \text{ M} = \text{N}_2$ no recommendation for k_f | 1.2 |

This evaluation accepts the recommendations in the review of Baulch, et al (1976)

REFERENCES

Baulch, D. L., Drysdale, D. L., Duxbury, J., and Grant, S. J., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 3: Homogeneous Gas Phase Reactions of the $\text{O}_2\text{-O}_3$ System, the $\text{C}_2\text{H}_2\text{-H}_2$ System, and of Sulphur-Containing Species," (Butterworths, London, 1976)

R. F. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Temp. Range/K | Reaction Rate Constant $k/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$ | Uncertainty Factor at 298K, notes |
|------|---|------------------|--|--------------------------------------|
| 1.46 | $\text{O} + \text{CO}_2 \rightarrow \text{CO} + \text{O}_2$ (1) | | $\Delta H(298) = 34 \text{ kJ/mol}$ | |
| 4.45 | $\text{O}_2 + \text{CO} \rightarrow \text{O} + \text{CO}_2$ (2) | | $k_1 = 2.8 \times 10^{-11} \exp(-26500/T)$ | 2 (a) |
| | Baulch, et al (1976) review | 1500-3000 | $k_2 = 4.2 \times 10^{-12} \exp(-24000/T)$ | 2 |
| | | 1500-3000 | (a) $k_2 = k_1 \exp$ | |

This evaluation accepts the recommendations in the review of Baulch, et al (1976)

REFERENCES

Baulch, D. L., Drysdale, D. D., Duxbury, J., and Grant, S. J., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 3: Homogeneous Gas Phase Reactions of the $\text{O}_2\text{-O}_3$ System, the $\text{CO-CO}_2\text{-H}_2$ System, and of Sulphur-Containing Species," (Butterworths, London, 1976)

R. F. Hampson
 May 1978

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Tempo Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncertainty Factor at 298K, notes |
|-------|--|------------------|--|--------------------------------------|
| | | | | |
| 1.46a | $O + CN \rightarrow CO + N$ Albers, et al (1975) Schmatjko, Wolfrum (1976) | 275-387 295 | $\Delta H (298) = -322 \text{ kJ/mol}$ 2.0×10^{-11} 1.8×10^{-11} | 104 |

This evaluation accepts the temperature independent result of Albers, et al (1975).
The room temperature result of Schmatjko and Wolfrum (1976) is in good agreement

REFERENCES

- Albers, E. A., Hoyermann, E., Schacke, E., Schmatjko, E. J., Wagner, E. G.,
and Wolfrum, J., "Absolute Rate Coefficients for the Reaction of H-Atoms
with N₂O and Some Reactions of CN Radicals," Symp. Combust. 15th
(Combustion Institute, Pittsburgh, 1975) 765-773
- Schmatjko, E. J., and Wolfrum, J., "Reaction of Flash Photolytically
Produced CN(X², v) Radicals with O(3p) Atoms," Photochem. Conference
12th (National Bureau of Standards, Washington, D. C. 20234 1976) RS-1
- E. F. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Uncertainty Factor
at 298K, notes

Reaction Rate Constant
 $k/cm^3 molecule^{-1} s^{-1}$

Tempo
Range/K

Reaction/Reference

No.

| | | | |
|------|--|-----|--|
| 1.47 | $O + CH_3 - CO_2 \cdot H$ (a) $- CO_2 \cdot H_2$ (b) Washida, et al (1974) | 297 | ΔH (298) = -462 kJ/mol = -358 kJ/mol $2.140 \pm 4 \times 10^{-10}$ ($k_a \pm k_b$) |
|------|--|-----|--|

Only reported value - no recommendation

REFERENCES

Washida, K., Martinez, P. I., and Hayes, K. D., "The Oxidation of Formyl
Radicals," Z. Naturforsch. A 29, 251-255 (1974)

P. F. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS
Reaction/Reference **Temp.** **Reaction Rate Constant** **Uncert. Factor**
Range/K **k/cm³ molecule⁻¹ s⁻¹** **at 298K, notes**

| No. | | | | |
|------|--|---------|---|------|
| 1.48 | $\text{O} + \text{CH}_2\text{O} \rightarrow \text{products}$ | | | 1.25 |
| | NASA (1979) eval | 200-300 | $3.2 \times 10^{-11} \exp(-1550 \pm 250)/T$ | |
| | Klemm (1979) | 250-498 | $(2.78 \pm 0.32) \times 10^{-11} \exp(-1525 \pm 40)/T$ | |
| | Klemm, et al (1979) | 298-748 | $(3.03 \pm 0.79) \times 10^{-11} \exp(-1554 \pm 125)/T$ | |
| | Chang, Barker (1979) | 296-437 | $(3.8 \pm 0.8) \times 10^{-11} \exp(-1583 \pm 73)/T$ | |
| | Herron, Penzhorn (1969) | 300 | 1.5×10^{-13} | |
| | Herron, Huie (1973) review | 300 | 1.5×10^{-13} | |
| | Mack, Thrush (1973) | 300 | 1.5×10^{-13} | |

The recommended values for A, E/R and k(298) are the averages of those determined by Klemm (1979) using flash photolysis - resonance fluorescence (250-498K), Klemm et al (1979) using discharge flow - resonance fluorescence (298-748K), and Chang and Barker (1979) using discharge flow - mass spectrometry (296-437K). All three studies are in good agreement. The k(298) value is also consistent with the results of Niki et al (1965), Herron and Penzhorn (1969) and Mack and Thrush (1973). While the mechanism for $\text{O} + \text{H}_2\text{CO}$ has been considered to be the abstraction reaction yielding $\text{OH} + \text{HCO}$, Chang and Barker suggest that an addition channel yielding $\text{H} + \text{HCO}_2$ may be occurring to the extent of 30% of the total reaction. This conclusion is based on an observation of CO_2 as a product of the reaction under conditions where reactions such as $\text{O} + \text{HCO} \rightarrow \text{H} + \text{CO}_2$ and $\text{O} + \text{HCO} \rightarrow \text{OH} + \text{CO}$ do not occur. This interesting suggestion needs independent confirmation.

REFERENCES

- Chang, J. S., and Barker, J. R., "Reaction Rate and Products for the Reaction $\text{O}(^3\text{P}) + \text{H}_2\text{CO}$," *J. Phys. Chem.* (submitted for publication, 1975)
- Herron, J. T., and Huie, R. E., "Rate Constants for the Reactions of Atomic Oxygen ($\text{O}(^3\text{P})$) with Organic Compounds in the Gas Phase," *J. Phys. Chem. Ref. Data* **2**, 467-518 (1973)
- Herron, J. T., and Penzhorn, R. D., "Mass Spectrometric Study of the Reactions of Atomic Oxygen with Ethylene and Formaldehyde," *J. Phys. Chem.* **73**, 191-196 (1969)
- Klemm, R. E., "Absolute Rate Parameters for the Reactions of Formaldehyde with C-Atoms and H-Atoms over the Temperature range 250-500K," *J. Chem. Phys.* **41**, 1927-1993 (1979)

Klemm, R. E., Skolnik, E. G., and Michael, J. V., Manuscript in preparation (1979)

Nach, G. P. R., and Thrush, E. A., "Reaction of Oxygen Atoms with Carbonyl Compounds. Part 1. Formaldehyde," *J. Chem. Soc., Faraday Trans 1* **69**, 208-215 (1973)

NASA (1979), Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," E. D. Hudson and E. I. Reed, Editors, Dec. 1975 (report of the June 1979 Harpers Ferry Workshop).

Niki, E., Daby, E. E., and Weinstock, E., "Mass Spectrometric Study of the Kinetics and Mechanism of the Ethylene-Atomic Oxygen Reaction by the Discharge-Flow Technique at 300°K," *Symp. Combust.* **12**, (Combustion Institute Pittsburgh, Pa., 1969) 277-285

R. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Uncertainty Factor
at 298K, notes

| No. | Reaction/Reference | Tempo Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncertainty Factor at 298K, notes |
|------|--|------------------|--|--------------------------------------|
| 1.49 | $\text{O} + \text{CH}_3 \rightarrow \text{CH}_2 + \text{H}$ (a) $\quad \quad \quad \text{O} + \text{CH}_3 \rightarrow \text{CH}_3 + \text{H}_2$ (b) | | | |
| | NASA (1979) eval | | | |
| | Washida, Bayes (1976) | 200-300 | $k_a = 1.0 \times 10^{-10} \exp(0.250/T)$ | 1.4 |
| | Washida, et al (1974) | 259-341 | $k_a = 1.0 \pm 0.2 \times 10^{-10}$ | |
| | | 300 | k_b negligible $k_b/k_a < 0.05$ | |
| | Slagle, Pruss, Gutman (1974) | 300 | $k_a = 1.85 \pm 0.28 \times 10^{-10}$ | |
| | Morris, Miki (1972) | 300 | $k_a/k(0) = \text{tetramethylethylene} = 1.5$ | |
| | Peeters, Mahnen (1973) | 1100-1900 | $k_a = 2.2 \times 10^{-10} \exp(-1000/T)$ | |
| | Bowman (1975) | 1875-2240 | $k_a = 1.7 \times 10^{-10}$ | |
| | Biordi, et al (1975) | 1550-1725 | $k_a = 1.7 \times 10^{-10}$ | |

This recommendation is based on the results of Washida and Bayes (1976). This reaction is probably only important in the vicinity of the stratosphere

REFERENCES

- Biordi, J. C., Lezzara, C. P., and Papp, J. E., "Flame Structure Studies of CF_3Br -Inhibited Methane Flames. II. Kinetics and Mechanisms," Symp Combust. 15th (Combustion Institute, Pittsburgh, 1975) 917-932
- Bowman, C. T., "Non-Equilibrium Radical Concentrations in Shock-Initiated Methane Oxidation," Symp Combust. 15th (Combustion Institute, Pittsburgh, 1975) 669-682
- Morris, E. D., Jr., and Miki, E., "Reaction of Methyl Radicals with Atomic Oxygen," Int. J. Chem. Kinet. 5, 47-53 (1972)
- NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," E. D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the June 1979 Harpers Ferry Workshop).
- Peeters, J., and Mahnen, G., "Reaction Mechanisms and Rate Constants of Elementary Steps in Methane-Oxygen Flames," Symp Combust. 14th (Combustion Institute, Pittsburgh, 1973) 133-141
- Slagle, I. R., Pruss, E. J., Jr., and Gutman, D., "Kinetics into the Steady State. I. Study of the Reaction of Oxygen Atoms with Methyl Radicals,"

Int. J. Chem. Kinet. **8**, 111-123 (1974)
Washida, M., and Bayes, K. D., "The Reactions of Methyl Radicals with Atomic
and Molecular Oxygen," Int. J. Chem. Kinet. **8**, 777-794 (1976)
Washida, M., Martinez, R. I., and Bayes, K. D., "The Oxidation of Formyl
Radicals," Z. Naturforsch. A **29**, 251-255 (1974)

P. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY

***** AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| Source/Reference | Temp. Range/K | Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$ | Uncert. Factor at 298K, notes |
|------------------|------------------|---|----------------------------------|
|------------------|------------------|---|----------------------------------|

| | | | |
|---------------|-----|-----------------------|--|
| (1979a) | 295 | 3.3×10^{-15} | |
|---------------|-----|-----------------------|--|

... reported value - no recommendation

REFERENCES

Seabell, L. M., and Goodman, K., "Reaction of $O(^3P)$ Atoms with Nitromethane
Vapour at 295 K," Chem. Phys. Lett. **54**, 105-108 (1979a)

B. F. Hampson
May 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Uncert. Factor
at 298K, notes

Reaction/Reference
Tempo
Range/K

Reaction Rate Constant
 $k/cm^3 molecule^{-1} s^{-1}$

No.

| | | | | |
|------|---|---------|-------------------------------------|--|
| 1.54 | $C + CH_3ONO \rightarrow products$ Davidson, Thrush (1975) | 300-410 | $2.2 \times 10^{-11} \exp(-2620/T)$ | |
|------|---|---------|-------------------------------------|--|

Only reported value - no recommendation

REFERENCES

Davidson, J. A., and Thrush, B. A., "Reaction of Oxygen Atoms with Methyl
and Ethyl Nitrites," J. Chem. Soc., Faraday Trans. 1 **71**, 2413-2420 (1975)

B. F. Hampson
May 1976

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Temp. Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncert. Factor at 298K, notes |
|------|--|------------------|--|----------------------------------|
| 1.56 | O + CH ₄ → products Herron, Huie (1973) review | 350-1000 | $3.5 \times 10^{-11} \exp (-4550/T)$ | 1.3 |

This evaluation accepts the recommendation in the review of Herron and Huie (1973)

REFERENCES

Herron, J. To. and Huie, R. E., "Rate Constants for the Reactions of Atomic Oxygen (³P) with Organic Compounds in the Gas Phase," J. Phys. Chem. Ref. Data 2, 467-518 (1973)

R. F. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Tempo Range/K | Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$ | Uncerto. Factor at 298K, notes |
|------|---|------------------|---|-----------------------------------|
| 1.57 | $C + C_2H_4 \rightarrow CH_3 + HCC (a)$ $\rightarrow CH_2CC + H_2 (b)$ | | $\Delta H (298) = -118 \text{ kJ/mol}$ $= -349 \text{ kJ/mol}$ | |
| | Herron, Huie (1973) evaluation | 200-500 | $5.5 \times 10^{-12} \exp(-565/T) (k_a + k_b)$ | 1.2 |
| | Pruss, Slagle, Gutsman (1974) | 300 | $k_b = 3.81 \pm 0.95 \times 10^{-14}$ $k_b/(k_a + k_b) = 0.05$ | (a) |
| | Atkinson, Pitts (1974) | 300-392 | $5.6 \times 10^{-12} \exp(-640 \pm 100/T) (k_a + k_b)$ | |
| | Singleton, Cvetanovic (1976) | 298-486 | $1.16 \times 10^{-11} \exp(-845/T)$ a) Calculated using above recommended value for $(k_a + k_b)$ | |

No recommendation

REFERENCES

- Atkinson, R., and Pitts, J. N., Jr., "Temperature Dependence of the Reaction Rate Constants for $O(^3P)$ Atoms with C_2H_4 , C_3H_6 , and $NO(M = N_2O)$, Determined by a Modulation Technique," *Chem. Phys. Lett.* **27**, 467-470 (1974)
- Herron, J. T., and Huie, R. E., "Rate Constants for the Reactions of Atomic Oxygen ($O(^3P)$) with Organic Compounds in the Gas Phase," *J. Phys. Chem. Ref. Data* **2**, 467-518 (1973)
- Pruss, F. J., Jr., Slagle, I. R., and Gutsman, D., "Determination of Branching Ratios for the Reaction of Oxygen Atoms with Ethylene," *J. Phys. Chem.* **78**, 663-665 (1974)
- Singleton, D. L., and Cvetanovic, R. J., "Temperature Dependence of the Reactions of Oxygen Atoms with Olefins," *J. Am. Chem. Soc.* **98**, 6812-6819 (1976)

F. F. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Temp. Range/K | Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$ | Uncert. Factor at 298K, notes |
|------|---|------------------|---|----------------------------------|
| 1.58 | $C + C_2H_6 \rightarrow$ products Herron, Huie (1973) evaluation | 300-650 | $4.1 \times 10^{-11} \exp (-3200/T)$ | 1.3 |

This evaluation accepts the recommendation in the review of Herron and Huie (1973)

REFERENCES

Herron, J. T., and Huie, R. E., "Rate Constants for the Reactions of Atomic Oxygen (O^3P) with Organic Compounds in the Gas Phase," *J. Phys. Chem. Ref. Data* 2, 467-518 (1973)

R. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Temp. Range/K | Reaction Rate Constant $k/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$ | Uncertainty Factor at 298K, notes |
|------|---|------------------|--|--------------------------------------|
| 1.59 | $\text{O} + \text{C}_3\text{H}_6 \rightarrow \text{products}$ | | | |
| | Herron, Eule (1973) evaluation | 200-500 | $4.1 \times 10^{-12} \exp(-38/T)$ | |
| | Atkinson, Pitts (1974) | 300-392 | $3.45 \times 10^{-12} \exp(0.4150/T)$ | |
| | Singleton, Cvetanovic (1976) | 298-483 | $1.26 \times 10^{-11} \exp(-363/T)$ | 1.2 |

No recommendation

REFERENCES

- Atkinson, R., and Pitts, J. N., Jr., "Temperature Dependence of the Reaction Rate Constants for $\text{d}(\text{3p})$ Atoms with C_2H_4 , C_3H_6 and $\text{NO}(\text{M} = \text{N}_2\text{O})$, Determined by a Modulation Technique," *Chem. Phys. Lett.* **21**, 467-470 (1974)
- Herron, J. T., and Eule, R. E., "Rate Constants for the Reactions of Atomic Oxygen (O^3p) with Organic Compounds in the Gas Phase," *J. Phys. Chem. Ref. Data* **2**, 467-518 (1973)
- Singleton, D. L., and Cvetanovic, R. J., "Temperature Dependence of the Reactions of Oxygen Atoms with Olefins," *J. Am. Chem. Soc.* **98**, 6812-6819 (1976)
- R. F. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Temp. Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncert. Factor at 298K, notes |
|------|---|------------------|--|----------------------------------|
| 1.60 | <p> $\text{C} \cdot \text{alkane} \rightarrow \text{H} \cdot + \text{alkyl radical}$ Herron, Hule (1969) </p> | 250-600 | <p> $k = [0.8 \exp(-2500/T) N_p + 2.2 \exp(-2250/T) N_s + 2.6 \exp(-1650/T) N_t] \times 10^{-11}$ Where N_p, N_s, and N_t are the number of primary, secondary, and tertiary hydrogen atoms, respectively. Do not use formula for CH_4. </p> | 3 |

This evaluation accepts the general rate expression developed by Herron and Hule (1969) which agrees with a large body of rate data to within a factor of 3

REFERENCES

- Herron, J. L., and Hule, R. E., "Rates of Reaction of Atomic Oxygen. II. Some C_2 to C_6 Alkanes," J. Phys. Chem. **73**, 3327-3337 (1969)
- R. F. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Temp. Range/K | Reaction Rate Constant $k/cm^3 \text{ molecule}^{-1} s^{-1}$ | Uncert. Factor at 258K, notes |
|-------|---|--|--|----------------------------------|
| 1.00a | $O + C_6H_6 \rightarrow \text{products}$ This survey Colussi, et al (1975) Atkinson, Pitts (1975a) Atkinson, Pitts (1979) | 300-420 258-462 300-392 299-440 | $1.6 \times 10^{-11} \exp(-2000/T)$ $1.8 \times 10^{-11} \exp(-2115/T)$ $1.6 \times 10^{-11} \exp(-2000/T)$ $1.7 \times 10^{-11} \exp(-2010/T)$ | 1.3 |

The recommended expression is derived from a least squares fit to the data points in these three studies

REFERENCES

- Atkinson, R., and Pitts, J. N., Jr., "Temperature Dependence of the Absolute Rate Constants for the Reaction of $O(^3P)$ Atoms with a Series of Aromatic Hydrocarbons over the Range 299-392°K," *J. Phys. Chem.* **79**, 295-297 (1975a)
- Atkinson, R., and Pitts, J. N., Jr., "Rate Constants for the Reaction of $O(^3P)$ Atoms with Benzene and Toluene over The Temperature Range 299-440 K," *Chem. Phys. Lett.* **53**, 485-489 (1979)
- Colussi, A. J., Singleton, D. L., Irwin, R. B., and Cvetanovic, R. J., "Absolute Rates of Oxygen (3P) Atom Reactions with Benzene and Toluene," *J. Phys. Chem.* **79**, 1900-1903 (1975)

R. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Temp. Range/K | Reaction Rate Constant $k/\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ | Uncerto. Factor at 298K, notes |
|-------|--|------------------|--|-----------------------------------|
| 1.60a | $\text{O} + \text{C}_6\text{H}_5\text{CH}_3 \rightarrow \text{products}$ | | | |
| | This survey | 300-460 | $2.4 \times 10^{-11} \text{ exp}(-1730/T)$ | 1.4 |
| | Colussi, et al (1975) | 298-462 | $3.8 \times 10^{-11} \text{ exp}(-1940/T)$ | |
| | Atkinson, Pitts (1975a) | 300-392 | $1.4 \times 10^{-11} \text{ exp}(-1560/T)$ | |
| | Atkinson, Pitts (1979) | 299-440 | $1.6 \times 10^{-11} \text{ exp}(-1530/T)$ | |

The recommended expression is derived from a least squares fit to the data points in these three studies

REFERENCES

- Atkinson, R., and Pitts, J. N., Jr., "Temperature Dependence of the Absolute Rate Constants for the Reaction of $\text{O}(^3\text{P})$ Atoms with a Series of Aromatic Hydrocarbons over the Range 299-392°K," J. Phys. Chem. **79**, 295-297 (1975a)
- Atkinson, R., and Pitts, J. N., Jr., "Rate Constants for the Reaction of $\text{O}(^3\text{P})$ Atoms with Benzene and Toluene over The Temperature Range 299-440 K," Chem. Phys. Lett. **63**, 485-489 (1979)
- Colussi, A. J., Singleton, D. L., Irwin, R. S., and Cvetanović, R. J., "Absolute Rates of Oxygen ($\text{O}(^3\text{P})$) Atom Reactions with Benzene and Toluene," J. Phys. Chem. **75**, 1900-1903 (1975)
- R. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| Reaction/Reference | Temp. Range/K | Reaction Rate Constant $k/\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ | Uncertainty Factor at 298K, notes |
|---|---------------|--|--------------------------------------|
| 1.64 | | | |
| $\phi + \text{CH}_3\text{Cl} \rightarrow \text{H}\phi + \text{CH}_2\text{Cl}$ | | $\Delta H (298) = -3 \text{ kJ/mol}$ | |
| Herron, Hule (1973) eval | 350-1000 | $2.6 \times 10^{-11} \text{ exp}(-3690/T)$ | 1.6 |
| Westenberg, deHaas (1975b) | 500-1000 | $5.8 \times 10^{-11} \text{ exp}(-4560/T)$ | (a) |
| Barassin, Combourieu (1974) | 298-443 | $2.2 \times 10^{-11} \text{ exp}(-3470/T)$ | |
| | | (a) Also measured $k(\phi + \text{CH}_3\text{Br})/k(\phi + \text{CH}_3\text{Cl})$ to be unity over same temp. range | |

This evaluation accepts the recommendation in the review of Herron and Hule (1973) with increased error limits to encompass the results of Barassin and Combourieu (1974)

REFERENCES

- Barassin, J., and Combourieu, J., "No. 1 - Etude Cinétique des Réactions entre l'Oxygène Atomique et les Dérivés Chlorés du Méthane, II. - Réactions $\text{CH}_3\text{Cl} + \phi$, $\text{CHCl}_3 + \phi$, $\text{CCl}_4 + \phi$ et $\text{CH}_4 + \phi$: Résultats Expérimentaux," *Bull. Soc. Chim. Fr.* 1-5 (1974)
- Herron, J. L., and Hule, R. E., "Rate Constants for the Reactions of Atomic Oxygen (O^3P) with Organic Compounds in the Gas Phase," *J. Phys. Chem. Ref. Data* 2, 467-518 (1973)
- Westenberg, A. A., and deHaas, N., "Reaction Rates of $\phi + \text{CH}_3\text{Br}$ and $\phi + \text{CH}_3\text{Cl}$," *J. Chem. Phys.* 52, 4477-4479 (1975b)
- F. F. Hampson
May 1976

Comments on the NASA(1979) recommended values for reactions of $\text{O}(^1\text{D})$ atoms

The recommendations adopt the time-resolved $\text{O}(^1\text{D})$ emission measurements at the National Geoscientific and Atmospheric Administration (NOAA) Laboratories for the reactions with H_2O , H_2 , CH_4 , N_2 , C_2 , O_3 , HCl , CFCl_3 , CF_2Cl_2 , NH_3 and CO_2 (Streit et al. (1976), Davidson et al. (1977) and Davidson et al. (1978).

Rate constants for all the above reactions (except the reaction with HCl) have also been measured at the Cambridge Laboratory (Heidner and Husain (1972), Heidner, Husain and Wiesenfeld (1973), and Fletcher and Husain (1976a, 1976b). These results are based on time resolved $\text{O}(^1\text{D})$ resonance absorption measurements. Data analysis used the modified Lambert-Beer law $I/I_0 = \exp(-\epsilon(\text{Cl})^{\gamma})$ where $\gamma = 0.41$.

The analysis of the latter results is less straightforward than that of the time resolved emission measurements since an independent calibration of the value of γ is required. Additionally, the results from the NOAA Laboratories for H_2O , CH_4 , N_2 , O_2 , O_3 and CO_2 have been confirmed very recently by a completely independent technique, Amisoto et al. (1978, 1979), although in this same study the value for N_2O is 40% higher than the result from the NOAA Laboratory. These same studies report significant quenching components in the reactions with N_2O , H_2O and CH_4 . Further studies are needed to confirm this result. New studies of $\text{O}(^1\text{D})$ reactions with O_2 and H_2O have been reported by Lee and Slanger (1978, 1979). These values are in good agreement with the results recommended here.

The branching ratio for the reaction of $\text{O}(^1\text{D})$ with N_2O to give $\text{N}_2 + \text{O}_2$ or $\text{NO} + \text{NO}$ is an average of the values reported by Davidson et al. (1979), Finkle et al. (1977) and the very recent result of Marx et al. (1979). This latest result is significantly different from the earlier results. Further study is needed. The branching ratio for reaction of $\text{O}(^1\text{D})$ with CH_4 to give $\text{CH} + \text{CH}_3$ or $\text{H}_2 + \text{CH}_2\text{O}$ is from Lin and DeMore (1973). The branching ratio for reaction of $\text{O}(^1\text{D})$ with O_3 to give $\text{O}_2 + \text{O}_2$ or $\text{O}_2 + \text{O} + \text{O}$ is from Davenport et al. (1974).

For the reactions of $\text{O}(^1\text{D})$ with CCl_2O , CFCl_2O and CF_2O , rate constants are reported only by the Cambridge Laboratory (Fletcher and Husain (1978)). Thus, for consistency, the recommended values for these rate constants had to be derived using a scaling procedure. This procedure preserves the relative placement of these rate constants among the set of Cambridge laboratory data but employs an average ratio (0.50) of the NOAA to Cambridge Laboratory rate constants for

these reactions studied by both groups. These reactions have been studied only at 298K. Based on consideration of similar $\phi(^1D)$ reactions, it is assumed that E/R equals zero, and therefore the value shown for the A-factor has been set equal to $k(298\text{ K})$. The chlorocarbon rate constants are for total disappearance of $\phi(^1D)$ and probably include physical quenching. Lower limits have been reported for the fraction of the total rate of disappearance of $\phi(^1D)$ proceeding through the reactive channel forming ClO for CFCl_3 (20.39) and CF_2Cl_2 (20.49) (Gillespie et al (1977)). It is not possible to give corresponding values for the reaction $\phi(^1D)$ with CCl_2O and CFClO . There are significant changes from the recommendations given in NASA SP-1010 for the values of the rate constants for the reactions of $\phi(^1D)$ with CF_2Cl_2 , CCl_2O , CFClO and CF_2O since the studies upon which the present recommendations are based did not exist at the time of the previous evaluations. There are changes in the values recommended for each of the reactive channels with N_2O based on new measurements of the branching ratio.

In view of the fact that there are two disparate sets of data and that the recommendations are based primarily on one of these, the error limits cited (1 σ) are somewhat larger than reported in the NOAA studies.

REFERENCES

- Amiseto, R. T., Force, A. P., and Wiesenfeld, J. E., "Ozone Photochemistry: Production and Deactivation of $O(2^1D_2)$ Following Photolysis at 248 nm," *Chem. Phys. Lett.* **58**, 40-43 (1978)
- Amiseto, R. T., Force, A. P., and Wiesenfeld, J. E., results presented at the National Meeting, American Chemical Society, Honolulu, April (1979)
- Bevenport, J. E., Schiff, E. I., and Welge, K. E., 1974 quoted in Cvetanovic, E. J., *Can. J. Chem.* **52**, 1452-1464 (1974)
- Davidson, J. A., Schiff, E. I., Stritt, G. E., McAfee, J. E., Schmittekepf, A. I., and Howard, C. J., "Temperature Dependence of $O(1D)$ Rate Constants for Reactions with N_2O , H_2 , CH_4 , HCl , and NH_3 ," *J. Chem. Phys.* **51**, 5021-5025 (1977)
- Davidson, J. A., Schiff, E. I., Brown, T. J., and Howard, C. J., "Temperature Dependence of the Rate Constants for Reactions of $O(1D)$ Atoms with a number of Halocarbons," *J. Chem. Phys.* **53**, 4277-4275 (1978)
- Davidson, J. A., Howard, C. J., Schiff, E. I., and Fehsenfeld, F. C., "Measurements of the Branching Ratios for the Reaction of $O(1D_2)$ with N_2O ," *J. Chem. Phys.* **10**, 1697-1704 (1979)
- Fletcher, I. S., and Husain, D., "The Collisional Quenching of Electronically Excited Oxygen Atoms, $O(1D_2)$ by the Gases NH_3 , H_2O , C_2H_6 , C_3H_8 , and $C(CH_3)_4$ Using Time-Resolved Attenuation of Atomic Resonance Radiation," *Can. J. Chem.* **55**, 1765-1770 (1976a)
- Fletcher, I. S., and Husain, D., "Absolute Reaction Rates of Oxygen(2^1D_2) with Halogenated Paraffins by Atomic Absorption Spectroscopy in the Vacuum Ultraviolet," *J. Phys. Chem.* **80**, 1837-1840 (1976b)
- Fletcher, I. S., and Husain, D., "The Collisional Quenching of $O(2^1D_2)$ by $COCl_2$, $COFCl$ and COF_2 using Atomic Absorption Spectroscopy in the Vacuum Ultraviolet," *J. Photochem. Sci.* **3**, 355-361 (1979)
- Gillespie, R. M., Garryay, J., and Donovan, E. J., "Reaction of $O(2^1D_2)$ with Halomethanes," *J. Photochem. Sci.* **2**, 29-40 (1977)

- Reider, R. P., III, and Husain, D., "Electronically Excited Oxygen Atoms, $O(^1D_2)$, A Time-Resolved Study of the Collisional Quenching by the Gases H_2 , D_2 , NO , N_2O , NO_2 , CH_4 , and C_2H_2 Using Atomic Absorption Spectroscopy in the Vacuum Ultraviolet," *Int. J. Chem. Kinet.* **5**, 819-831 (1973)
- Reider, R. P., III, Husain, D., and Wiesenfeld, J. P., "Kinetic Investigation of Electronically Excited Oxygen Atoms, $O(^1D_2)$, by Time-Resolved Attenuation of Atomic Resonance Radiation in the Vacuum Ultra-violet, Part 2.-Collisional Quenching by the Atmospheric Gases N_2 , O_2 , CO , CO_2 , H_2O and O_3 ," *J. Chem. Soc., Faraday Trans. II* **69**, 927-938 (1973)
- Lee, L. C., and Slinger, T. G., "Observations on $O(^1D - 3p)$ and $O_2(b^1\Sigma - X^3\Sigma^-)$ Following O_2 Photodissociation," *J. Chem. Phys.* **48**, 4053-4060 (1978)
- Lee, L. C., and Slinger, T. G., "Atmospheric OH Production-The $O(^1D) + H_2O$ Reaction Rate," *Geophys. Res. Lett.* **5**, 165-166 (1978)
- Lin, C.-L., and DeMore, W. B., "Reactions of $O(^1D)$ with Methane and Ethane," *J. Phys. Chem.* **77**, 863-865 (1973a)
- Marx, W., Bahr, F., and Schurath, U., "The NO Yield of $O(^1D) + N_2O$ as Function of Kinetic Energy," *Ber. Bunsenges. Phys. Chem.* **83**, 225-230 (1979)
- NASA RP-1010, "Chlorofluoromethanes and the Stratosphere" R. D. Hudson, Editor, August 1977 This reference contains the NASA (1977) rate constant recommendations.
- NASA (1979), Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," R. D. Hudson and R. L. Reed, Editors, Deco 1979 (report of the June 1975 Harper Ferry Workshop)
- Parkle, R. J., Veltreuer, R. M., Felder, W., and Fontijn, A., 1977, "Measurements on $O(^1D)/N_2O$ and HO_2/O_3 Kinetics," Report No. FAA-AEQ-77-10, prepared for High Altitude Pollution Program, U.S. Department of Transportation, Washington, D.C., June, 1977
- Streit, G. E., Howard, C. J., Schmeltekopf, A. L., Davidson, J. A., and Schiff, H. I., "Temperature Dependence of $O(^1D)$ Rate Constants for Reactions with O_2 , N_2 , CO_2 , O_3 , and H_2O ," *J. Chem. Phys.* **65**, 4761-4764 (1976)

AD-A091 631

NATIONAL BUREAU OF STANDARDS WASHINGTON DC CHEMICAL --ETC F/G 4/1
CHEMICAL KINETIC AND PHOTOCHEMICAL DATA SHEETS FOR ATMOSPHERIC --ETC /
APR 80 R F HAMPSON DOT-FA79WAI-005

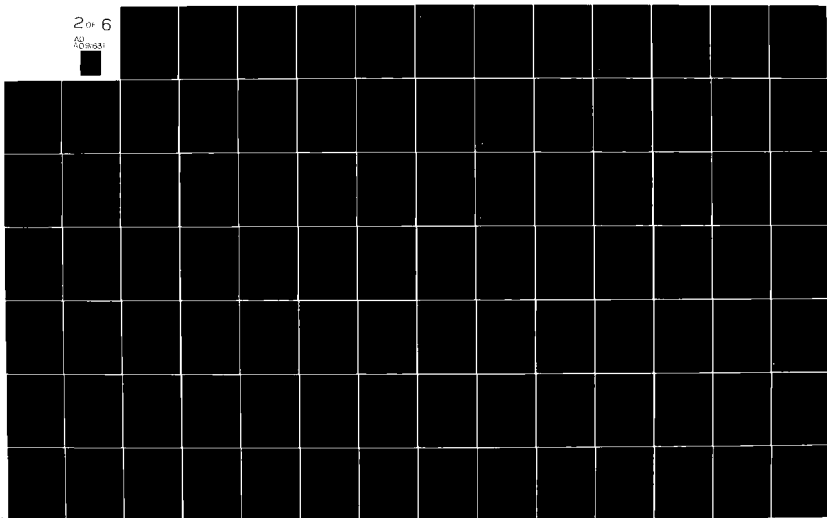
UNCLASSIFIED

FAA/EE-80-17

NL

2 of 6

AD-A091 631



CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Temp. Range/K | Reaction Rate Constant $k/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$ | Uncertainty Factor at 298K, notes |
|-----|---|------------------|---|--------------------------------------|
| 2.4 | $\text{O}(^1\text{D}_2) + \text{O}_2 \rightarrow \text{O}_2(^1\Sigma_g^+) + \text{O}(^3\text{P})$ NASA (1979) eval | 200-300 298 | $\text{AH}(298) = -33 \text{ kJ/mol}$ $2.9 \times 10^{-11} \exp((67850)/T)$ 3.6×10^{-11} | 1.3 |
| | Streit, et al (1976) | 104-354 | $(2.9 \pm 0.6) \times 10^{-11} \exp(67/T)$ | |
| | Fletcher, Husain (1976a) | 300 | $(5.3 \pm 0.6) \times 10^{-11}$ | |
| | Lee, Slanger (1978) | 298 | $(4.0 \pm 0.6) \times 10^{-11}$ | |
| | Asimoto, et al (1979) | 298 | $(4.2 \pm 0.2) \times 10^{-11}$ | |

See comments on NASA (1979) recommended values for reactions of $\text{O}(^1\text{D})$ atoms

REFERENCES

- Asimoto, S. T., Force, A. P., and Wiesenfeld, J. R., results presented at the National Meeting, American Chemical Society, Honolulu, April (1979)
- Fletcher, I. S., and Husain, D., "The Collisional Quenching of Electronically Excited Oxygen Atoms, $\text{O}(^1\text{D}_2)$ by the Gases NH_3 , H_2O , C_2H_6 , C_3H_8 , and $\text{C}(\text{CH}_3)_4$ Using Time-Resolved Attenuation of Atomic Resonance Radiation," Can. J. Chem. **54**, 1765-1770 (1976a)
- Lee, L. C., and Slanger, T. G., "Observations on $\text{O}(^1\text{D} - ^3\text{P})$ and $\text{O}_2(^1\Sigma_g^+ - \text{X } ^3\Sigma_g^-)$ Following O_2 Photodissociation," J. Chem. Phys. **53**, 4053-4060 (1978)
- NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," R. D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the June 1979 Harpers Ferry Workshop).
- Streit, G. E., Howard, C. J., Schmeltkeopf, A. L., Davidson, J. A., and Schiff, H. I., "Temperature Dependence of $\text{O}(^1\text{D})$ Rate Constants for Reactions with O_2 , N_2 , CO_2 , O_3 , and H_2O ," J. Chem. Phys. **55**, 4761-4764 (1976)

P. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Temp. Range/K | Reaction Rate Constant $k/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$ | Uncertainty Factor at 298K, notes |
|-----|---|------------------|--|--------------------------------------|
| 2.7 | $\sigma(^1D_2) + O_3 \rightarrow O_2 + O_2$ (a) $\rightarrow O_2 + 2O$ (b) | | | |
| | NASA (1979) eval | 200-300 | ΔH (298) = -582 kJ/mol = -83 kJ/mol $k_a = 1.2 \times 10^{-10} \exp((0.450)/T)$ $k_b = 1.2 \times 10^{-10} \exp((0.450)/T)$ | 1.3 1.3 |
| | Streit, et al (1976) | 103-393 | $(2.4 \pm 0.5) \times 10^{-10} (k_a + k_b)$ | |
| | Reidner, et al (1973) | 300 | $(2.7 \pm 0.2) \times 10^{-10} (k_a + k_b)$ | |
| | Cvetanovic (1974) review | 300 | $k_a/k_b \sim 1$ | |
| | Arimoto, et al (1978) | 298 | $(2.4 \pm 0.1) \times 10^{-10} (k_a + k_b)$ | |

See comments on NASA (1979) recommended values for reactions of $D(^1D)$ atoms

REFERENCES

- Aminote, S. T., Force, A. P., and Wiesenfeld, J. R., "Ozone Photochemistry: Production and Deactivation of $O(2H_2)$ Following Photolysis at 248 nm." *Chem. Phys. Lett.* 60, 40-43 (1978)

Cvetanovic, R. J., "Excited State Chemistry in the Stratosphere,"

Cano, J. *Chem.* 52, 1452-1466 (1974)

Heigener, R. F., III, Eusain, D., and Wiesenfeld, J. R., "Kinetic Investigation of Electronically Excited Oxygen Atoms, $O(^1D_2)$, by Time-Resolved Attenuation of Atomic Resonance Radiation in the Vacuum Ultra-violet, Part 2.-Collisional Quenching by the Atmospheric Gases N_2 , O_2 , CO ,

CDs, H₂O and G₂." J. Chem. Soc., Faraday Trans. II **69**, 927-938 (1973)

WASA (1979)². Recommendations of the NASA Panel for Data Evaluation,

published in NASA RP 1049 "The Stratosphere: Present and Future."

Re D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the

June 1979 Harpers Ferry Workshop).

Streit, G. Es, Howard, Co Jo, Schmeltekopf, A. Lo, Davidson, J. A., and

Schiff, H. I., "Temperature Dependence of $\phi(^1D)$ Rate Constants for

Reactions with O_2 , N_2 , CO_2 , O_3 , and H_2O ." J. Chem. Phys. 65.

4761-4764 (1976)

R. F. Hampton

June 1979

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Temp. Range/K | Reaction Rate Constant $k/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$ | Uncert. Factor at 298K, notes |
|-----|--|------------------|---|----------------------------------|
| 2.9 | $\text{O}(^1\text{D}_2) + \text{N}_2 \rightarrow \text{N}_2 + \text{O}(^3\text{P})$ This survey Reidner, Husain (1973) | 300 300 | $\Delta H(298) = -190 \text{ kJ/mol}$ 4.2×10^{-11} $(8.5 \pm 1.0) \times 10^{-11}$ | 2 |

The recommended value has been derived from the reported value by use of the scaling factor 0.50 for consistency with other recommended $\text{O}(^1\text{D})$ rates. See comments on NASA (1979) recommended values for reactions of $\text{O}(^1\text{D})$ atoms

REFERENCES

Reidner, R. F., III, and Husain, D., "Electronically Excited Oxygen Atoms, $\text{O}(^1\text{D}_2)$, A Time-Resolved Study of the Collisional Quenching by the Gases H_2 , D_2 , N_2 , N_2O , NO_2 , CH_4 , and C_2H_2 Using Atomic Absorption Spectroscopy in the Vacuum Ultraviolet," *Int. J. Chem. Kinetics* **5**, 819-831 (1973)

R. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Temp. Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncert. Factor at 298K, notes |
|------|---|------------------|--|----------------------------------|
| 2.10 | $O(^1D_2) + NO_2 \rightarrow NO + O_2$ This survey Weidner, Husain (1973) | 300 300 | $\Delta H (298) = -382 \text{ kJ/mol}$ 1.2×10^{-10} $(2.3 \pm 0.2) \times 10^{-10}$ | 2 |

The recommended value has been derived from the reported value by use of the scaling factor 0.50 for consistency with other recommended $O(^1D)$ rates. See comments on NASA (1979) recommended values for reactions of $O(^1D)$ atoms

REFERENCES

Weidner, R. F., III, and Husain, D., "Electronically Excited Oxygen Atoms, $O(^1D_2)$, A Time-Resolved Study of the Collisional Quenching by the Gases H_2 , D_2 , NO , N_2O , NO_2 , CH_4 , and C_3H_2 Using Atomic Absorption Spectroscopy in the Vacuum Ultraviolet," Int. J. Chem. Kinet. **5**, 819-831 (1973)

R. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Temp Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncertainty Factor at 298K, notes |
|------|---|-----------------|--|--------------------------------------|
| 2.12 | $O(^1D_2) + N_2 \rightarrow N_2 + O(^3P)$ | | | |
| | NASA (1979) eval | 200-300 | $\Delta H (298) = -150 \text{ kJ/mol}$ $2.0 \times 10^{-11} \exp((107 \pm 50)/T)$ | |
| | Streit, et al (1976) | 298 | 2.9×10^{-11} | |
| | Heidner, et al (1973) | 104-354 | $(2.0 \pm 0.4) \times 10^{-11} \exp(107/T)$ | 1.3 |
| | Amimoto, et al (1975) | 300 | $(6.9 \pm 0.6) \times 10^{-11}$ | |
| | | 258 | $(2.9 \pm 0.1) \times 10^{-11}$ | |

See comments on NASA (1979) recommended values for reactions of $O(^1D)$ atoms

REFERENCES

- Amimoto, S. T., Forster, A. P., and Wiesenfeld, J. R., results presented at the National Meeting, American Chemical Society, Honolulu, April (1979)
- Heidner, R. F., III, Husain, D., and Wiesenfeld, J. R., "Kinetic Investigation of Electronically Excited Oxygen Atoms, $O(^1D_2)$, by Time-Resolved Attenuation of Atomic Resonance Radiation in the Vacuum Ultra-Violet. Part 2.-Collisional Quenching by the Atmospheric Gases N_2 , O_2 , CO , CO_2 , H_2O and H_2 ," J. Chem. Soc., Faraday Trans. II 69, 927-936 (1973)
- NASA (1979), Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," R. D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the June 1975 Barbers Ferry Workshop).
- Streit, G. E., Howard, C. J., Schmeltzer, A. L., Davidson, J. A., and Schiff, H. I., "Temperature Dependence of $O(^1D)$ Rate Constants for Reactions with O_2 , N_2 , CO , CO_2 , H_2O , and H_2 ," J. Chem. Phys. 55, 4761-4764 (1976)

R. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Temp. Range/K | Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$ | Uncert. Factor at 298K, notes |
|-------|--|------------------|---|----------------------------------|
| 2.12M | $O(^1D_2) + N_2 + M \rightarrow N_2^+ + M$ | | $\Delta H(298) = -357 \text{ kJ/mol}$ | |
| | NASA (1979) eval | 200-300 | $3.5 \times 10^{-37} (T/300)^{-0.45} \text{ cm}^3 \text{ molecule}^{-2} s^{-1}$ | 5 |
| | Kajimoto, Cvitanovic (1976) | 256 | 3.5×10^{-37} | (a) |
| | Gaetke, et al (1973) | 258 | 3×10^{-36} | |
| | Simenowitz, et al (1972) | 298 | $< 2 \times 10^{-36}$ | (a) |
| | | | (a) adjusted value based on $k(O(^1D) + N)$ this survey | |

This recommendation is based on the results reported in Kajimoto and Cvitanovic (1976)

REFERENCES

- Gaetke, R., Glazer, E., Rippler, E., Luther, E., and
Tree, J., "Addition Reactions of Oxygen Atoms at High
Pressures," Symp. Combust. 14 (Combustion Institute,
Pittsburgh, 1973) 295-303
- Kajimoto, G., and Cvitanovic, R. J., "Formation of Nitrous Oxide in the
Reaction of $O(^1D_2)$ Atoms with Nitrogen," J. Chem. Phys. 64, 1005-1015
(1976)
- NASA (1979), Recommendations of the NASA Panel for Data Evaluation,
published in NASA RP 1049 "The Stratosphere: Present and Future,"
R. D. Hudson and E. L. Reed, Editors, Dec. 1979 (report of the
June 1979 Harpers Ferry Workshop).
- Simenowitz, R., Linn, E., and Reichlen, J., "On the Production
of N_2^+ from the Reaction of $O(^1D)$ with N_2 ," J. Geophys.
Res. 77, 4248-4250 (1972)

R. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Tempo Range/K | Reaction Rate Constant $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | Uncert. Factor at 298K, notes |
|------|--|---------------|---|----------------------------------|
| 2.13 | $\text{d}^1\text{D}_2 + \text{N}_2\text{C} - \text{N}_2 + \text{C}^1\text{D}_2$ (a) - 2ND (b) NASA (1979) eval | 200-300 | $\Delta H (298) = -521 \text{ kJ/mol}$ $= -340 \text{ kJ/mol}$ $k_a = 4.8 \times 10^{-11} \exp((0.450)/T)$ $k_b = 6.2 \times 10^{-11} \exp((0.450)/T)$ | 1.5 1.5 |
| | Davidson, et al (1977) | 204-355 | $(1.1 \pm 0.2) \times 10^{-10} (k_a + k_b)$ | |
| | Heidner, Husain (1973) | 300 | $(2.2 \pm 0.2) \times 10^{-10} (k_a + k_b)$ | |
| | Amimoto, et al (1979) | 258 | $(1.5 \pm 0.1) \times 10^{-10} (k_a + k_b)$ | |
| | Davidson, et al (1979) | 170-434 | $k_a/k_b = (0.72 \pm 0.11) \cdot (21.6 \pm 7)/T$ | |
| | Pirkle, et al (1977) | 290 | $k_a/k_b = 0.92 \pm 0.10$ | |
| | Marx, et al (1979) | 298 | $k_a/k_b = 0.62 \pm 0.04$ | |

See comments on NASA (1979) recommended values for reactions of d^1D atoms

REFERENCES

- Amimoto, S. To., Force, A. P., and Wiesenfeld, J. R., results presented at the National Meeting, American Chemical Society, Honolulu, April (1979)
- Davidson, J. A., Howard, C. J., Schiff, H. I., and Fehsenfeld, F. C., "Measurements of the Branching Ratios for the Reaction of d^1D_2 with N_2O ," *J. Chem. Phys.* **70**, 1697-1704 (1979)
- Davidson, J. A., Schiff, H. I., Streit, G. E., McAfee, J. R., Schmeltekopf, A. L., and Howard, C. J., "Temperature Dependence of d^1D Rate Constants for Reactions with N_2O , H_2 , CH_4 , HCl , and NH_3 ," *J. Chem. Phys.* **67**, 5021-5025 (1977)
- Heidner, R. F., III, and Husain, D., "Electronically Excited Oxygen Atoms, $\text{O}(^1\text{D}_2)$, A Time-Resolved Study of the Collisional Quenching by the Gases H_2 , D_2 , HD , N_2O , ND_2 , CH_4 , and C_2D_2 Using Atomic Absorption Spectroscopy in the Vacuum Ultraviolet," *Int. J. Chem. Kinet.* **5**, 819-831 (1973)
- Marx, W., Bahe, F., and Schurath, U., "The NO Yield of O^1D + N_2O as Function of Kinetic Energy," *Ber. Bunsenges. Phys. Chem.* **83**, 225-230 (1979)
- NASA (1979), Recommendations of the NASA Panel for Data Evaluation,

published in NASA EP 1049 "The Stratosphere: Present and Future,"
R. D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the
June 1979 Barbers Perry Workshop).

Pinkle, R. J., Volltrauer, R. N., Felder, W., and Fentim, A.,
1977, "Measurements on $\text{O}(\text{D})/\text{H}_2\text{O}$ and HO_2/O_3 Kinetics,"
Report No. FAA-AEQ-77-10, Prepared for High Altitude
Pollution Program, U.S. Department of Transportation,
Washington, D.C., June, 1977

P. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Temp. Range/K | Reaction Rate Constant $k/cm^3 \text{ molecule}^{-1} s^{-1}$ | Uncertainty Factor at 298K, notes |
|------|--|---------------------------|--|--------------------------------------|
| 2.17 | $O(^1D_2) + NH_3 \rightarrow NH_2 + H_2$ NASA (1979) eval Davidson, et al (1977) Fletcher, Hudson (1976a) | 200-300 204-354 300 | $\Delta H (298) = -169 \text{ kJ/mol}$ $2.5 \times 10^{-10} \exp(0.50/T)$ $(2.5 \pm 0.5) \times 10^{-10}$ $(6.3 \pm 0.7) \times 10^{-10}$ | 1.3 |

See comments on NASA (1979) recommended values for reactions of $O(^1D)$ atoms

REFERENCES

- Davidson, J. A., Schiff, H. I., Streit, G. E., McAfee, J. E.,
Schmeltekopf, A. L., and Howard, C. J., "Temperature Dependence of
 $O(^1D)$ Rate Constants for Reactions with N_2O , H_2 , CH_4 , HCl , and NH_3 ,"
J. Chem. Phys., **67**, 5021-5025 (1977)
- Fletcher, I. S., and Hudson, D., "The Collisional Quenching of Electronically
Excited Oxygen Atoms, $O(^1D_2)$ by the Gases NH_3 , H_2O , C_2H_6 , C_3H_8 , and
 $C(CH_3)_4$ Using Time-Resolved Attenuation of Atomic Resonance Radiation,"
Can. J. Chem., **54**, 1765-1770 (1976a)
- NASA (1979). Recommendations of the NASA Panel for Data Evaluation,
published in NASA RP 1049 "The Stratosphere: Present and Future,"
R. D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the
June 1979 Harpers Ferry Workshop).

R. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Tempo Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncerto. Factor at 298K, notes |
|------|---|---------------------------|--|-----------------------------------|
| 2.21 | $\text{O}(^1\text{D}_2) + \text{H}_2 \rightarrow \text{H} + \text{H}$ NASA (1979) eval Davidson, et al (1977) Weidner, Husain (1973) | 200-300 204-352 300 | $\Delta H (298) = -182 \text{ kJ/mol}$ $9.9 \times 10^{-11} \exp((0.50)/T)$ $(9.9 \pm 3.0) \times 10^{-11}$ $(2.7 \pm 0.3) \times 10^{-10}$ | 1.3 |

See comments on NASA (1979) recommended values for reactions of $\text{O}(^1\text{D})$ atoms

REFERENCES

- Davidson, J. A., Schiff, H. I., Streit, G. E., McAfee, J. R., Schmeltekopf, A. L., and Howard, C. J., "Temperature Dependence of $\text{O}(^1\text{D})$ Rate Constants for Reactions with N_2O , H_2 , CH_4 , HCl , and NH_3 ," J. Chem. Phys. **57**, 5021-5025 (1977)
- Weidner, R. F., III, and Husain, D., "Electronically Excited Oxygen Atoms, $\text{O}(^1\text{D}_2)$, A Time-Resolved Study of the Collisional Quenching by the Gases H_2 , D_2 , N_2 , N_2O , N_2 , CH_4 , and C_3H_2 Using Atomic Absorption Spectroscopy in the Vacuum Ultraviolet," Int. J. Chem. Kinet. **5**, 819-831 (1973)
- NASA (1979), Recommendations of the NASA Panel for Data Evaluation, published in NASA EP 1049 "The Stratosphere: Present and Future," R. D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the June 1979 Harpers Ferry Workshop).

R. F. Hampson
June 1979

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Temp. Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncert. Factor at 298K, notes |
|------|---------------------------------------|------------------|--|----------------------------------|
| 2.22 | $\sigma(^1D_2) + H_2 \rightarrow 2HD$ | | | |
| | NASA (1979) eval | 200-300 | $2.3 \times 10^{-10} \exp((0.50)/T)$ | 1.3 |
| | Streit, et al (1976) | 253-353 | $(2.3 \pm 0.4) \times 10^{-10}$ | |
| | Heidner, et al (1973) | 300 | $(3.0 \pm 0.3) \times 10^{-10}$ | |
| | Lee, Slanger (1979) | 300 | $(2.6 \pm 0.5) \times 10^{-10}$ | |
| | Amimoto, et al (1979) | 298 | $(2.0 \pm 0.3) \times 10^{-10}$ | |

See comments on NAEA (1979) recommended values for reactions of $d(^1D)$ atoms

REFERENCES

- Asimoto, S., To. Force, A. Po., and Wiesenfeld, Jo Po., results presented at the National Meeting, American Chemical Society, Honolulu, April (1979)
- Beidner, R. Po., III, Husain, Do., and Wiesenfeld, Jo Po., "Kinetic Investigation of Electronically Excited Oxygen Atoms, $O(^1D_2)$, by Time-Resolved Attenuation of Atomic Resonance Radiation in the Vacuum Ultra-violet, Part 2.-Collisional Quenching by the Atmospheric Gases N_2 , O_2 , CO, CO_2 , H_2O and O_3 ," J. Chem. Soc., Faraday Trans. II 69, 927-938 (1973)
- Lee, Lo. Ca., and Slinger, To. Go., "Atmospheric Oh Production--The $O(^1D) + H_2O$ Reaction Rate," Geophys. Res. Lett. 6, 165-166 (1979) NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," R. De Hudson and E. Lo. Reed, Editors, Dec. 1979 (report of the June 1979 Harpers Ferry Workshop).
- Streit, Go. Eo., Howard, Co. Jo., Schmeltekopf, A. Lo., Davidson, Jo. A., and Schiff, H. Lo., "Temperature Dependence of $O(^1D)$ Rate Constants for Reactions with O_2 , N_2 , CO, CO_2 , O_3 , and H_2O ," J. Chem. Phys. 65, 4761-4764 (1976)

R. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Temp. Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncert. Factor at 298K, notes |
|------|---|------------------|--|----------------------------------|
| | | | | |
| 2.23 | $\phi(^1D_2) + H_2O_2 \rightarrow H_2O + HO_2$ This survey Fletcher, Husain (1976a) | 300 300 | $\Delta H (298) = -262 \text{ kJ/mol}$ 2.6×10^{-10} $(5.2 \pm 0.6) \times 10^{-10}$ | 2 |

The recommended value has been derived from the reported value by use of the scaling factor 0.50 for consistency with other recommended $\phi(^1D)$ rates. See comments on NASA (1979) recommended values for reactions of $\phi(^1D)$ atoms

REFERENCES

Fletcher, I. S., and Husain, D., "The Collisional Quenching of Electronically Excited Oxygen Atoms, $\phi(^1D_2)$ by the Gases NH_3 , H_2O_2 , C_2H_6 , C_3H_8 , and $C(CH_3)_4$ Using Time-Resolved Attenuation of Atomic Resonance Radiation," Can. J. Chem. **54**, 1765-1770 (1976a)

P. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Uncert. Factor
at 298K, notes

Reaction Rate Constant
k/cm³molecule⁻¹s⁻¹

Temp.
Range/K

Reaction/Reference

No.

| | | | | |
|------|--|--------------------|--|-----|
| 2.39 | $O(^1D_2) + HCl \rightarrow H^{\delta} + Cl$ NASA (1979) eval Davidson, et al (1977) | 200-300 199-379 | $\Delta H (298) = -166 \text{ kJ/mol}$ $1.4 \times 10^{-10} \exp((0.250)/T)$ $(1.4 \pm 0.4) \times 10^{-10}$ | 1.3 |
|------|--|--------------------|--|-----|

See comments on NASA (1979) recommended values for reactions of $O(^1D)$ atoms

REFERENCES

- Davidson, J. A., Schiff, H. L., Strick, G. E., McIver, J. E.,
 Schmeltkeopf, A. L., and Howard, C. J., "Temperature Dependence of
 $O(^1D)$ Rate Constants for Reactions with N_2O , H_2 , CH_4 , HCl , and NH_3 ,"
 J. Chem. Phys. 67, 5021-5025 (1977)
 NASA (1979). Recommendations of the NASA Panel for Data Evaluation,
 published in NASA TP 1049 "The Stratosphere: Present and Future,"
 R. D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the
 June 1979 Harpers Ferry Workshop).

K. P. Hampson
 June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Uncert. Factor
at 298K, notes

Reaction/Reference
Temp.
Range/K

Reaction Rate Constant
 $\text{m}^3/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

No.

$\text{O}(^1\text{D}_2) + \text{HF} \rightarrow \text{H} + \text{F}$
 NASA (1979) eval

200-300

$\Delta H (298) = -47 \text{ kJ/mol}$
 $1 \times 10^{-10} \exp((0 \pm 100)/T)$

3

New entry. No experimental data. k is assumed to be comparable to most other
 old rate constants which approach the gas kinetic collision frequency, and as
 such is not expected to exhibit a strong temperature dependence.

REFERENCES

NASA (1979). Recommendations of the NASA Panel for Data Evaluation,
 published in NASA SP 1049 "The Stratosphere: Present and Future,"
 P. D. Hudson and E. I. Reed, Editors, Deco 1979 (report of the
 June 1979 Harpers Ferry Workshop).

R. F. Hampson
 June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Temp. Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncert. Factor at 298K, notes |
|------|---|------------------|--|----------------------------------|
| 2.45 | O(¹ D ₂) + CO → CO + O(³ P) Davidson, et al (1978a) Heidner, et al (1973) | 113-323 300 | ΔH (298) = -150 kJ/mol (4.7±0.9) × 10 ⁻¹¹ exp(63/T) (7.3±0.7) × 10 ⁻¹¹ | 1.4 |

This evaluation accepts the results of the temperature dependent study of Davidson, et al (1978a)

REFERENCES

- Davidson, J. A., and Schlif, E. I., "Temperature Dependence of the Deactivation of O(¹D) by CO from 113-323 K," J. Chem. Phys. **69**, 1216-1217 (1978a)
- Heidner, R. F., III, Busala, D., and Wiesenfeld, J. E., "Kinetic Investigation of Electronically Excited Oxygen Atoms, O(¹D₂), by Time-resolved Attenuation of Atomic Resonance Radiation in the Vacuum Ultra-violet. Part 2.-Collisional Quenching by the Atmospheric Gases N₂, O₂, CO, CO₂, H₂O and O₃," J. Chem. Soc., Faraday Trans. II **69**, 927-938 (1973)

R. F. Hampson
 June 1979

CHEMICAL KINETICS DATA SURVEY
 PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Temp. Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncert. Factor at 298K, notes |
|------|---|------------------|---|----------------------------------|
| 2.46 | $\phi(^1D_2) + C_2 \rightarrow C_2 + \phi(^3P)$ NASA (1979) eval | 200-300 258 | $\Delta H (298) = -190 \text{ kJ/mol}$ $6.8 \times 10^{-11} \exp((117450)/T)$ 1.0×10^{-10} | 1.3 |
| | Streit, et al (1976) | 139-200 | 1.2×10^{-10} | |
| | Fletcher, Bursin (1976a) | 200-354 | $(6.8 \pm 1.4) \times 10^{-11} \exp(117/T)$ | |
| | Animoto, et al (1975) | 300 298 | $(1.7 \pm 0.2) \times 10^{-10}$ $(1.28 \pm 0.07) \times 10^{-10}$ | |

See comments on NASA (1979) recommended values for reactions of $\phi(^1D)$ atoms

REFERENCES

- Animoto, S. T., Force, A. P., and Wiesenfeld, J. R., results presented at the National Meeting, American Chemical Society, Honolulu, April (1979)
- Fletcher, I. S., and Bursin, D., "The Collisional Quenching of Electronically Excited Oxygen Atoms, $\phi(^1D_2)$ by the Gases NH_3 , H_2O , C_2H_6 , C_3H_8 , and $C(CH_3)_4$ Using Time-Resolved Attenuation of Atomic Resonance Radiation," *Can. J. Chem.* **54**, 1765-1770 (1976a)
- NASA (1979), Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," P. D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the June 1979 Harpers Ferry Workshop).
- Streit, O. E., Howard, C. J., Schmeltekopf, A. L., Davidson, J. A., and Schiff, H. I., "Temperature Dependence of $\phi(^1D)$ Rate Constants for Reactions with C_2 , H_2 , CO_2 , O_3 , and N_2O ," *J. Chem. Phys.* **55**, 4761-4764 (1976)

R. F. Hampson
 June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Tempo Range/K | Reaction Rate Constant $k/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$ | Uncerto. Factor at 298K, notes |
|------|---|------------------|--|-----------------------------------|
| 2,56 | $\text{O}(^1\text{D}_2) + \text{CH}_4 \rightarrow \text{CH}_3 + \text{HC} \text{ (a)}$ $\text{O}(^1\text{D}_2) + \text{CH}_4 \rightarrow \text{CH}_2 + \text{H}_2 \text{ (b)}$ | | $\Delta H(298) = -180 \text{ kJ/mol}$ $= -473 \text{ kJ/mol}$ | |
| | NASA (1979) eval | 200-300 | $k_a = 1.3 \times 10^{-10} \exp((0 \pm 50)/T)$ $k_b = 1.4 \times 10^{-11} \exp((0 \pm 50)/T)$ | 1.3 1.3 |
| | Davidson, et al (1977) | 198-357 | $(1.4 \pm 0.4) \times 10^{-10} (k_a + k_b)$ | |
| | Reidner, Husain (1973) | 300 | $(3.0 \pm 0.4) \times 10^{-10} (k_a + k_b)$ | |
| | Animoto, et al (1979) | 298 | $(1.57 \pm 0.14) \times 10^{-10} (k_a + k_b)$ | |
| | Lin and DeMore (1973) | 295 | $k_b/k_a = 0.1$ | |

See comments on NASA (1979) recommended values for reactions of $\text{O}(^1\text{D})$ atoms

REFERENCES

- Animoto, S. T., Force, A. P., and Wiesenfeld, J. R., results presented at the National Meeting, American Chemical Society, Honolulu, April (1979)
- Davidson, J. A., Schiff, H. L., Streit, G. R., McAfee, J. R., Schaefer, A. L., and Howard, C. J., "Temperature Dependence of $\text{O}(^1\text{D})$ Rate Constants for Reactions with N_2O , H_2 , CH_4 , HCl , and NH_3 ," *J. Chem. Phys.* **67**, 5021-5025 (1977)
- Reidner, R. P., III, and Husain, D., "Electronically Excited Oxygen Atoms, $\text{O}(^1\text{D}_2)$, A Time-Resolved Study of the Collisional Quenching by the Gases H_2 , D_2 , N_2 , N_2O , CH_4 , and C_2H_2 Using Atomic Absorption Spectroscopy in the Vacuum Ultraviolet," *Int. J. Chem. Kinet.* **5**, 819-831 (1973)
- Lin, C. C., and DeMore, W. B., "Reactions of $\text{O}(^1\text{D})$ with Methane and Ethane," *J. Phys. Chem.* **77**, 863-869 (1973)
- NASA (1979), Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," R. D. Hudson and E. L. Reed, Editors, Dec. 1979 (report of the June 1979 Harpers Ferry Workshop).

P. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Temp. Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncert. Factor at 298K, notes |
|------|--|------------------|--|----------------------------------|
| 2.58 | O(¹ D ₂) + C ₂ H ₆ → products This survey Fletcher, Husain (1976a) | 300 300 | 3.6 x 10 ⁻¹⁰ (7.3±0.8) x 10 ⁻¹⁰ | 2 |

The recommended value has been derived from the reported value by use of the scaling factor 0.50 for consistency with other recommended O(¹D) rates. See comments on NASA (1979) recommended values for reactions of O(¹D) atoms

REFERENCES

Fletcher, I. S., and Husain, D., "The Collisional Quenching of Electronically Excited Oxygen Atoms. O(²D₂) by the Gases NH₃, H₂O₂, C₂H₆, C₃H₈, and C(CH₃)₄ Using Time-Resolved Attenuation of Atomic Resonance Radiation," Can. J. Chem. **54**, 1765-1770 (1976a)

R. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Temp. Range/K | Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$ | Uncert. Factor at 298K, notes |
|------|--|---------------------------|---|----------------------------------|
| 2.61 | $O(^1D_2) + CF_2Cl_2 \rightarrow$ products NASA (1979) eval Davidson, et al (1978) Fletcher, Husain (1976b) | 200-300 173-343 300 | $1.4 \times 10^{-10} \exp((0 \pm 50)/T)$ $(1.45 \pm 0.5) \times 10^{-10}$ $(4.6 \pm 0.5) \times 10^{-10}$ | 1.3 |

See comments on NASA (1979) recommended values for reactions of $O(^1D)$ atoms

REFERENCES

- Davidson, J. A., Schiff, A. I., Brown, T. J., and Howard, C. J.,
 "Temperature Dependence of the Rate Constants for Reactions
 of $O(^1D)$ Atoms with a number of Halocarbons," J. Chem.
 Phys. **52**, 4277-4278 (1978)
- Fletcher, I. S., and Husain, D., "Absolute Reaction Rates of Oxygen(2^1D_2)
 with Halogenated Paraffins by Atomic Absorption Spectroscopy in
 the Vacuum Ultraviolet," J. Phys. Chem. **80**, 1837-1840 (1976b)
- NASA (1979). Recommendations of the NASA Panel for Data Evaluation,
 published in NASA RP 1049 "The Stratosphere: Present and Future,"
 E. D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the
 June 1975 Harpers Ferry Workshop).
- Y. F. Hampson
 June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Temp. Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncert. Factor at 298K, notes |
|------|---|---------------------------|---|----------------------------------|
| 2.62 | O(¹ D ₂) + CFCl ₃ - products NASA (1979) eval Davidson, et al (1978) Fletcher, Husain (1976b) | 200-300 173-343 300 | 2.2 x 10 ⁻¹⁰ exp((0±50)/T) (2.2±0.7) x 10 ⁻¹⁰ (5.5±0.7) x 10 ⁻¹⁰ | 1.3 |

See comments on NASA (1979) recommended values for reactions of O(¹D) atoms

REFERENCES

- Davidson, J. A., Schiff, A. I., Brown, T. J., and Howard, C. J.,
"Temperature Dependence of the Rate Constants for Reactions
of O(¹D) Atoms with a number of Halocarbons," J. Chem.
Phys. **69**, 4277-4275 (1978)
- Fletcher, I. S., and Husain, D., "Absolute Reaction Rates of Oxygen(²D₂)
with Halogenated Paraffins by Atomic Absorption Spectroscopy in
the Vacuum Ultraviolet," J. Phys. Chem. **80**, 1837-1840 (1976b)
- NASA (1979). Recommendations of the NASA Panel for Data Evaluation,
published in NASA RP 1049 "The Stratosphere: Present and Future,"
R. D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the
June 1979 Harpers Ferry Workshop).
- R. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Temp. Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncert. Factor at 298K, notes |
|------|---|------------------|--|----------------------------------|
| 2.65 | O(¹ D ₂) + CCl ₂ → products NASA (1979) eval Fletcher, Husain (1978) | 200-300 300 | 3.6 x 10 ⁻¹⁰ exp((0±50)/T) (7.1±0.9) x 10 ⁻¹⁰ | 1.4 |

See comments on NASA (1979) recommended values for reactions of O(¹D) atoms

REFERENCES

- Fletcher, I. S., and Husain, D., "The Collisional Quenching of O(²D₂) by CCl₂, CCl₂ and CCl₂ using Atomic Absorption Spectroscopy in the Vacuum Ultraviolet," *J. Photochem.* **2**, 355-361 (1978)
- NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," R. D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the June 1979 Harpers Ferry Workshop).

R. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Temp. Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncert. Factor at 298K, notes |
|------|--|------------------|--|----------------------------------|
| 2.65 | O(¹ D ₂) + CFC16 - products NASA (1979) eval Fletcher, Husain (1978) | 200-300 300 | 1.9 x 10 ⁻¹⁰ exp((0±50)/T) (3.7±0.4) x 10 ⁻¹⁰ | 1.4 |

See comments on NASA (1979) recommended values for reactions of O(¹D) atoms

REFERENCES

- Fletcher, I. S., and Husain, D., "The Collisional Quenching of O(²D₂) by CCl₂, CFC1 and CDF₂ using Atomic Absorption Spectroscopy in the Vacuum Ultraviolet," J. Photochem. 8, 355-361 (1978)
- NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," P. D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the June 1979 Harpers Ferry Workshop).

P. P. Hampson
 June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Temp. Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncertainty Factor at 298K, notes |
|------|--|------------------|--|--------------------------------------|
| 2.65 | $O(^1D_2) + CF_2O \rightarrow$ products NASA (1979) eval Fletcher, Husain (1978) | 200-300 300 | $2.3 \times 10^{-10} \exp((0.450)/T)$ (4.6 ± 0.4) $\times 10^{-10}$ | 1.4 |

See comments on NASA (1979) recommended values for reactions of $O(^1D)$ atoms

REFERENCES

- Fletcher, I. E., and Husain, D., "The Collisional Quenching of $O(^1D_2)$ by $COCl_2$, CCl_4 and COF_2 using Atomic Absorption Spectroscopy in the Vacuum Ultraviolet," J. Photochem. 8, 355-361 (1978)
- NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," R. D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the June 1979 Harpers Ferry Workshop).
- R. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Temp. Range/K | Reaction Rate Constant $k/cm^3 \text{ molecule}^{-1} s^{-1}$ | Uncertainty Factor at 298K, notes |
|-----|--|------------------|---|--------------------------------------|
| 3.1 | $O(^1S) + O(^3P) \rightarrow \text{products}$ Slanger, Black (1976a) Schofield (1978) review | 200-365 250 | $5 \times 10^{-11} \exp(-305/T)$ 1.6×10^{-11} | 1.5 |

This evaluation accepts the results of the temperature dependent study of Slanger and Black (1976a). The room temperature value is the same as that recommended in Schofield's (1978) review. It is three orders of magnitude greater than the value calculated by Krauss and Neumann (1975) for the specific channel yielding $2 O(^1D)$, suggesting the importance of other channels

REFERENCES

- Krauss, M., and Neumann, D., "On The Interaction of $O(^1S)$ with $O(^3P)$,"
Chem. Phys. Lett. **36**, 372-374 (1975)
- Schofield, K., "Rate Constants for the Gaseous Interactions of
 $O(^1D_2)$ and $O(^2^1S_0)$ - A Critical Evaluation," J. Photochem.
2, 55-68 (1978)
- Slanger, T. G., and Black, G., " $O(^1S)$ Quenching by $O(^3P)$," J. Chem.
Phys. **64**, 3763-3766 (1976a)
- P. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Uncert. Factor
at 298K, notes

Reaction/Reference
Temp.
Range/K
Reaction Rate Constant
 $k/\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$

No.

| | | | | | |
|-----|---|---------|------------------------------------|--|-----|
| 3.4 | $\text{O}(^1\text{S}) + \text{O}_2 \rightarrow \text{products}$ | | | | |
| | Slanger, Welge (1973) review | 200-377 | $4.3 \times 10^{-12} \exp(-250/T)$ | | |
| | Schofield (1978) review | 298 | 2.6×10^{-13} | | 1.4 |

This evaluation accepts the recommendation of Slanger and Welge (1973). Slanger and Black (1978b) measured the branching ratio for the production of $\text{O}(^1\text{D})$ and $\text{O}(^3\text{P})$. The fraction yielding $\text{O}(^1\text{D})$ is 0.31 \pm 0.07, the remainder yielding $\text{O}(^3\text{P})$.

REFERENCES

- Schofield, L., "Rate Constants for the Gaseous Interactions of $\text{O}(^2\text{D})$ and $\text{O}(^2\text{S})$ - A Critical Evaluation," *J. Photochem.* **2**, 55-68 (1978)
- Slanger, T. G., and Black, G., "Products of the $\text{O}(^1\text{S}) - \text{O}_2$ Interaction," *J. Chem. Phys.* **55**, 998-1000 (1978b)
- Slanger, T. G., and Welge, K. H., "Rate Constants for Reactions of $\text{O}(^1\text{S})$," in *Chemical Kinetics Data Survey V. Sixty-six Contributed Rate and Photochemical Data Evaluation on Ninety-four Reactions*, NBSIR 73-206, D. Garvin, Ed., National Bureau of Standards, Washington, D.C., (1973) pages 22-32

T. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Temp. Range/°K | Reaction Rate Constant $k/\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ | Uncert. Factor at 298K, notes |
|-----|--|-------------------|--|----------------------------------|
| 3.7 | $\text{O}(^1\text{S}) + \text{O}_3 \rightarrow \text{products}$ Schofield (1978) review | 258 | 5.6×10^{-10} | 1.4 |

This evaluation accepts the recommendation in Schofield's (1978) review with increased error limits. The same value was recommended in the review of Slanger and Welge (1973)

REFERENCES

- Schofield, L., "Rate Constants for the Gaseous Interactions of $\text{O}(^1\text{D}_2)$ and $\text{O}(^2^1\text{S}_0)$ - A Critical Evaluation," J. Photochem. 2, 55-68 (1978)
- Slanger, T. G., and Welge, K. E., "Rate Constants for Reactions of $\text{O}(^1\text{S})$," in Chemical Kinetics Data Survey V. Sixty-six Contributed Rate and Photochemical Data Evaluations on Ninety-four Reactions, NBSIR 73-206, D. Garvin, Ed., National Bureau of Standards, Washington, D.C., (1973) pages 22-32

R. F. Hampson
 June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Uncert. Factor
at 298K, notes

Reaction/Reference

Temp.
Range/K

Reaction Rate Constant
k/cm³molecule⁻¹s⁻¹

No.

| | | | | |
|-----|--|----------------|---|-----|
| 3.9 | $\phi(^1S) + M_0 \rightarrow \text{products}$ Slanger, Welge (1973) review Schofield (1978) review | 200-300 298 | 3.2×10^{-11} (1) 0.5 5.7×10^{-10} | 1.2 |
|-----|--|----------------|---|-----|

This evaluation accepts the recommendation of Slanger and Welge (1973) which agrees with Schofield's (1978) recommendation at room temperature. Slanger and Black (1978a) measured the branching ratio for the production of $\phi(^1D)$ and $\phi(^3P)$. The fraction yielding $\phi(^1D)$ is 0.6480.06, the remainder yielding $\phi(^3P)$.

REFERENCES

Schofield, K., "Rate Constants for the Gaseous Interactions of $\phi(^1D_2)$ and $\phi(^2\Sigma_0)$ - A Critical Evaluation," J. Photochem. 2, 55-66 (1978)

Slanger, T. G., and Black, G., " $\phi(^1S)$ Interactions - The Product Channels," J. Chem. Phys. 68, 989-997 (1978a)

Slanger, T. G., and Welge, K. H., "Rate Constants for Reactions of $\phi(^1S)$," in Chemical Kinetics Data Survey V, Sixty-six Contributed Rate and Photochemical Data Evaluations on Ninety-four Reactions, NBSIR 73-206, D. Garvin, Ed., National Bureau of Standards, Washington, D.C., (1973) pages 22-32

F. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Temp. Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncert. Factor at 298K, notes |
|------|---|------------------|--|----------------------------------|
| 3.10 | $\text{O}(^1\text{S}) + \text{NO}_2 \rightarrow \text{products}$ Schofield (1978) review | 258 | 5×10^{-10} | 1.5 |

This evaluation accepts the recommendation in Schofield's (1978) review. The same value was recommended in the review of Slanger and Welge (1973)

REFERENCES

- Schofield, K., "Rate Constants for the Gaseous Interactions of $\text{O}(^1\text{D}_2)$ and $\text{O}(^2^1\text{S}_0)$ - A Critical Evaluation," *J. Photochem.* **2**, 55-68 (1978)
- Slanger, T. G., and Welge, K. H., "Rate Constants for Reactions of $\text{O}(^1\text{S})$," in *Chemical Kinetics Data Survey V. Sixty-six Contributed Rate and Photochemical Data Evaluations on Ninety-four Reactions*, NBSIR 73-206, D. Garvin, Ed., National Bureau of Standards, Washington, D.C., (1973) pages 22-32

R. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Temp. Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncertainty Factor at 298K, notes |
|------|--|------------------|--|--------------------------------------|
| | | | | |
| 3.12 | O(¹ S) + N ₂ → products | | | |
| | Sclanger, Welge (1973) review | 200-380 | 4.5×10^{-17} | |
| | Schofield (1978) review | 250 | 4.5×10^{-17} | |

This evaluation accepts the recommendation in the review of Sclanger and Welge (1973)

REFERENCES

- Schofield, K., "Rate Constants for the Gaseous Interactions of O(²P₂) and O(²S₀) - A Critical Evaluation," J. Photochem. 2, 55-68 (1978)
- Sclanger, T. G., and Welge, K. H., "Rate Constants for Reactions of O(¹S)," in Chemical Kinetics Data Survey V, Sixty-six Contributed Rate and Photochemical Data Evaluations on Ninety-four Reactions, NBSIR 73-206, D. Garvin, Ed., National Bureau of Standards, Washington, D.C., (1973) pages 22-32

P. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY
 PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Temp. Range/K | Reaction Rate Constant $k/\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ | Uncert. Factor at 298K, notes |
|------|--|------------------|--|----------------------------------|
| 3.13 | $\text{O}(^1\text{S}) + \text{N}_2\text{O} \rightarrow \text{products}$ Slanger, Black (1976b) Schofield (1978) review | 200-368 258 | $3.6 \times 10^{-11} \exp(-420/T)$ 9.4×10^{-12} | 1.3 |

This evaluation accepts the results of the temperature dependent study of Slanger and Black (1976b). The room temperature value is the same as that recommended in Schofield's (1978) review. Slanger and Black (1978a) measured the relative importance of the interaction pathways. The fraction yielding $\text{O}(^1\text{D})$ is 0.33±0.07, the remainder yielding $\text{O}(^3\text{P})$, with no chemical reaction

REFERENCES

- Schofield, K. "Rate Constants for the Gaseous Interactions of $\text{O}(^1\text{D}_2)$ and $\text{O}(^2^1\text{S}_0)$ - A Critical Evaluation," J. Photochem. 2, 55-62 (1978)
- Slanger, T. G., and Black, G., "Temperature Dependence for Quenching of $\text{O}(^1\text{S})$ by N_2O ," J. Chem. Phys. 55, 2025-2026 (1976b)
- Slanger, T. G., and Black, G., " $\text{O}(^1\text{S})$ Interactions - The Product Channels," J. Chem. Phys. 55, 989-997 (1978a)
- R. F. Hampson
 June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Uncertainty Factor
at 298K, notes

| Reaction/Reference | Temp. Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncertainty Factor at 298K, notes |
|--|------------------------------|--|--------------------------------------|
| 3.17 O(¹ S) + NH ₃ → products Schofield (1978) review | 258 5 × 10 ⁻¹⁰ | | 1.5 |

This evaluation accepts the recommendation in Schofield's (1978) review.
The same value was recommended in the review of Slanger and Welge (1973)

REFERENCES

- Schofield, K., "Rate Constants for the Gaseous Interactions of
O(²D₂) and O(²P₂) - A Critical Evaluation," J. Photochem.
2, 55-66 (1978)
- Slanger, T. G., and Welge, L. E., "Rate Constants for Reactions of O(¹S),"
in Chemical Kinetics Data Survey V, Sixty-six Contributed Rate and Photo-
chemical Data Evaluations on Ninety-four Reactions, NBSIR 73-206, D. Garvin,
Ed., National Bureau of Standards, Washington, D.C., (1973) pages 22-32
- V. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Temp. Range/K | Reaction Rate Constant $k/\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ | Uncertainty Factor at 298K, notes |
|------|--|------------------|--|--------------------------------------|
| 3.22 | $\text{O}(^1\text{S}) + \text{H}_2\text{O} \rightarrow \text{products}$ + Schofield (1978) review | 258 | 5×10^{-10} | 3 |

This evaluation accepts the recommendation in Schofield's (1978) review with increased error limits. Slanger and Black (1978a) measured the relative importance of the interaction pathways. The fraction yielding $\text{O}(^1\text{D})$ is 0.30±0.06, that yielding $\text{O}(^3\text{P})$ is 0.69±0.06, with the major fraction (0.61±0.06) being the chemical interaction to give $\text{OH} + \text{OH}$.

REFERENCES

- Schofield, K., "Rate Constants for the Gaseous Interactions of $\text{O}(^1\text{D}_2)$ and $\text{O}(^2^1\text{S}_0)$ - A Critical Evaluation," J. Photochem. Q. 55-68 (1978)
- Slanger, T. G., and Black, G., " $\text{O}(^1\text{S})$ Interactions - The Product Channels," J. Chem. Phys. 68, 589-997 (1978a)
- E. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Uncert. Factor
at 298K, notes

| No. | Reaction/Reference | Tempo Range/K | Reaction Rate Constant $k/\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ | Uncert. Factor at 298K, notes |
|------|--|------------------|--|----------------------------------|
| 3.46 | $\text{O}(^1\text{S}) + \text{C}_2\text{H}_2 \rightarrow \text{products}$ Slanger, Welge (1973) review Schofield (1976) review | 200-450 250 | $3 \times 10^{-11} \exp(-1320/T)$ 3.6×10^{-13} | 10.4 |

This evaluation accepts the recommendation in the review of Slanger and Welge (1973) which agrees with Schofield's (1978) recommendation at room temperature. Slanger and Black (1978a) measured the branching ratio for the production of $\text{O}(^1\text{D})$ and $\text{O}(^3\text{P})$. The fraction yielding $\text{O}(^1\text{D})$ is 0.63 ± 0.05 , the remainder yielding $\text{O}(^3\text{P})$.

REFERENCES

- Schofield, K., "Rate Constants for the Gaseous Interactions of $\text{O}(^1\text{D}_2)$ and $\text{O}(^1\text{S}_0)$ - A Critical Evaluation," *J. Photochem.* **2**, 55-68 (1976)
- Slanger, T. G., and Black, G., " $\text{O}(^1\text{S})$ Interactions - The Product Channels," *J. Chem. Phys.* **62**, 589-997 (1978a)
- Slanger, T. G., and Welge, K. E., "Rate Constants for Reactions of $\text{O}(^1\text{S})$," in *Chemical Kinetics Data Survey V. Sixty-six Contributed Rate and Photochemical Data Evaluations on Ninety-four Reactions*, NBSIR 73-206, D. Garvin, Ed., National Bureau of Standards, Washington, D.C., (1973) pages 22-32

P. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Temp. Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncertainty Factor at 298K, notes |
|------|--|------------------|--|--------------------------------------|
| 3.56 | O(¹ S) + CH ₄ → products Schofield (1978) review | 298 | 2.7 x 10 ⁻¹⁴ | 2.5 |

This evaluation accepts the recommendation in Schofield's (1978) review with increased error limits

REFERENCES

Schofield, K., "Rate Constants for the Gaseous Interactions of
O(²D₂) and O(²S₀) - A Critical Evaluation," J. Photochem.
2, 55-68 (1978)

P. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Temp. Range/K | Reaction Rate Constant $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | Uncert. Factor at 298K, notes |
|-----|--|------------------|--|----------------------------------|
| 4.8 | $\text{O}_2 + \text{N} \rightarrow \text{NO} + \text{O} (2)$ | | $\Delta H (298) = -133 \text{ kJ/mol}$ | |
| 1.9 | $\text{O} + \text{NO} \rightarrow \text{O}_2 + \text{N} (2)$ | | | |
| | NASA (1979) eval | 280-300 | $k_f = 4.4 \times 10^{-12} \exp(-3220/340/T)$ | 1.25 |
| | C6DATA (1979) eval | 280-333 | $k_f = 4.4 \times 10^{-12} \exp(-3220/350/T)$ | 1.25 |
| | Becker, Groth, Kley (1969) | 280-333 | $k_f = 5.5 \times 10^{-12} \exp(-3220/T)$ | |
| | Clyne, Thrush (1961) | 412-755 | $k_f = 1.4 \times 10^{-11} \exp(-3570/T)$ | |
| | Wilson (1967) | 300-910 | $k_f = 2.3 \times 10^{-11} \exp(-3975/T)$ | |
| | Clark, Wayne (1970) | 302 | $k_f = 10.8 \times 10^{-17}$ | |
| | Westenberg, et al (1970) | 298 | $k_f = 7.5 \times 10^{-17}$ | |
| | Taylor (1975) | 2000-10000 | $k_f = 2.2 \times 10^{-14} (T) \exp(-3560/T)$ | |
| | Baulch, et al (1973) review | 1000-3000 | $k_f = k_f/K_{eq} = 2.5 \times 10^{-15} (T) \exp(-19500/T)$ | 2 |

Activation energy based on Becker et al (1969). Value and uncertainty at 298 K assigned from average of Clyne and Thrush (1961), Wilson (1967), Becker et al (1969), Clark and Wayne (1970) and Westenberg et al (1970). The recommendation in NASA RP-1010 was purely the Becker expression. Inclusion of the other 298 K data results in the lower pre-exponential factor of the present recommendation. Independent confirmation of the temperature dependence is needed

REFERENCES

- Baulch, D. L., Drysdale, D. D., and Horne, D. G., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 2: Homogeneous Gas Phase Reactions of the H_2 - N_2 - O_2 System," (Butterworths, London, 1973)
- Becker, K. E., Groth, W., and Kley, D., "The Rate Constant of the Aeronomic Reaction $\text{N} + \text{O}_2$," *Z. Naturforsch.* A **24**, 1280-1281 (1969)
- Clark, I. D., and Wayne, R. P., "Kinetics of the Reaction between Atomic Nitrogen and Molecular Oxygen in the Ground ($^3\Sigma_g^-$) and First Excited ($^1\Delta_g$) States," *Proc. Roy. Soc. London A* **316**, 539-550 (1970)
- Clyne, M. A. A., and Thrush, B. A., "Kinetics of the Reaction of Active Nitrogen with Oxygen and with Nitric Oxide," *Proc. Roy. Soc. Lond. A* **261**, 259-273 (1961)
- C6DATA(1979). Recommendations of the C6DATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.
- NASA RP-1010. "Chlorofluoromethanes and the Stratosphere"

- R. D. Hudson, Editor, August 1977 This reference contains the NASA (1977) rate constant recommendations, NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," R. D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the June 1979 Barbers Ferry Workshop).
- Taylor, R. L., "High Temperature Reactions of Air" pages 5-154 to 5-157 in "The Natural Stratosphere of 1974" Climatic Impact Assessment Program Monograph 1, DOT-TST-75-51, Department of Transportation, Washington D.C., September 1975
- Vestenberg, A. A., Roscoe, J. M., and DeHaas, M., "Rate Measurements on $N + O_2(1A_g) \rightarrow NO + O$ and $H + O_2(1A_g) \rightarrow OH + O$," Chem. Phys. Lett. **42**, 597-599 (1978)
- Wilson, W. E., "Rate Constant for the Reaction $N + O_2 \rightarrow NO + O$," J. Chem. Phys. **45**, 2017-2018 (1967)
- W. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No | Reaction/Reference | Temp. Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncert. Factor at 298K, notes |
|--------|--|------------------|---|----------------------------------|
| 4.9, 9 | O ₂ + NO + NO → NO ₂ + NO ₂ (f) | | ΔH (298) = -114 kJ/mol | |
| 10, 10 | NO ₂ + NO ₂ → NO + NO + O ₂ (r) | 273-660 | k _f = 3.3 × 10 ⁻³⁹ exp(530/T) cm ⁶ molecule ⁻² s ⁻¹ | 1.5 |
| | *Baulch, et al (1973) review | 600-2000 | k _r = 3.3 × 10 ⁻¹² exp(-13500/T) cm ³ molecule ⁻¹ s ⁻¹ | 1.4 |
| | Stedman, Niki (1973) | 300 | k _f = 2.0 × 10 ⁻³⁶ | |

This evaluation accepts the recommendations in the review of Baulch, et al (1973)

REFERENCES

- Baulch, D. L., Drysdale, D. D., and Horne, D. G., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 2: Homogeneous Gas Phase Reactions of the H₂-N₂-O₂ System," (Butterworths, London, 1973)
- Stedman, D. H., and Niki, S., "Kinetics and Mechanism for the Photolysis of Nitrogen Dioxide in Air," J. Phys. Chem. **77**, 2604-2609 (1973)
- R. F. Hampson
 May 1978

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Uncert Factor
at 298K, notes

Reaction Rate Constant
k/cm³ molecule⁻¹ s⁻¹

Temp.
Range/K

Reaction/Reference

No

ΔH (298) = - 19 kJ/mol
No recommendation

O₂ + NO + M → NO₂ + M
Baulch, et al (1973) review

4.9H

See the review of Baulch, et al (1973) for a discussion of reported results. However, there is no direct evidence for the occurrence of this reaction and no recommendation can be made

REFERENCES

Baulch, D. L., Drysdale, D. D., and Horne, D. G., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 2: Homogeneous Gas Phase Reactions of the H₂-M₂-O₂ System," (Butterworths, London, 1973)

D. F. Hampson
May 1976

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Uncert. Factor
at 298K, notes

Reaction Rate Constant
k/cm³molecule⁻²s⁻¹

Temp.
Range/K

Reaction/Reference

No

| | | | | | |
|-------------------|--|------------------------|--|--|-----|
| 4,10M | O ₂ + B + M → NO ₂ + M (2) | ΔH (298) = -216 kJ/mol | | | |
| 2 ^o ,M | NO ₂ + M → O ₂ + B + M (r) | | | | |
| | NASA (1979) eval | | | | |
| | 200-300 | | | | |
| | CGDATA (1979) eval | | | | |
| | 200-400 | | | | |
| | Eurylo (1972) | | | | 1.6 |
| | 203-404 | | | | |
| | Wong, Davis (1974) | | | | |
| | 220-360 | | | | |
| | 300-2000 | | | | |
| | Baulch, et al (1972) eval | | | | |
| | 300 | | | | |
| | Bishop, Dorfman (1970) | | | | |
| | 300 | | | | |
| | Hixie, Eyre, Dorfman (1971) | | | | |
| | 300 | | | | |
| | Ahumada, Michael, Osborne (1972) | | | | |
| | 300 | | | | |
| | Vestenberg, deHaas (1972a) | | | | |
| | 300 | | | | |
| | Slack (1977) | | | | |
| | 980-1176 | | | | (a) |
| | 964-1075 | | | | (b) |
| | 200-2000 | | | | (c) |
| | 200-2200 | | | | |

REFERENCES

- Ahumada, Jo J., Michael, J., Vo., and Osborne, D. To., "Pressure Dependence and Third Body Effects on the Rate Constants for H + O₂, H + NO, and H + CO," J. Chem. Phys. **52**, 3736-3745 (1972)
- Baulch, D. L., Drysdale, D. D., Horne, D. G., and Lloyd, A. Co., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 1: Homogeneous Gas Phase Reactions of the H₂-O₂ System," (Butterworths, London, 1972)
- Bishop, W. P., and Dorfman, L. M., "Pulse Radiolysis Studies. XVI: Kinetics of the Reaction of Gaseous Hydrogen Atoms with Molecular Oxygen by Fast Lyman-α Absorption Spectrophotometry," J. Chem. Phys. **52**, 3210-3216 (1970)
- CGDATA(1979): Recommendations of the CGDATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data

Minde, T. G., Jr., and Dorfman, L. M., "Pulse Radiolysis Studies: IX Kinetics of Some Addition Reactions of Gaseous Hydrogen Atoms by Fast Lyman- α Absorption Spectrophotometry," *J. Chem. Phys.* **55**, 3422-3428 (1971)

Kurylo, W. J., "Absolute Rate Constants for the Reaction $H + O_2 + M \rightarrow H_2O + M$ Over the Temperature Range 203-404 K," *J. Phys. Chem.* **76**, 3518-3526 (1972)

NASA (1979) Recommendations of the NASA Panel for Data Evaluation, published in NASA SP 1049 "The Stratosphere: Present and Future," R. D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the June 1979 Harpers Ferry Workshop).

Slack, M. W., "Rate Coefficient for $H + O_2 + M \rightarrow H_2O + M$ Evaluated from Shock Tube Measurements of Induction Times," *Combust. Flame* **28**, 241-245 (1977)

Wentenberg, A. A., and deHaas, M., "Steady-State Intermediate Concentrations and Rate Constants: Some H_2 Results," *J. Phys. Chem.* **76**, 1586-1593 (1972a)

Wong, K., and Davis, D. D., "A Flash Photolysis-Resonance Fluorescence Study of the Reaction of Atomic Hydrogen with Molecular Oxygen: $H + O_2 + M \rightarrow H_2O + M$," *Int. J. Chem. Kinet.* **6**, 401-416 (1974)

R. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No | Reaction/Reference | Temp. Range/K | Reaction Rate Constant $\text{m}^3/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | Uncert. Factor at 298K, notes |
|------|---|------------------|--|----------------------------------|
| 4.24 | $\text{O}_2 + \text{HNO} \rightarrow \text{NO} + \text{HO}_2$ Demerjian, et al (1974) review | 300 | $\Delta H (298) = - 7 \text{ kJ/mol}$ $\pm 2 \times 10^{-20}, \text{ E/E} > 5000\text{K}$ | |

No data; estimated value

REFERENCES

- Demerjian, L. L., Kerr, J., A., and Calvert, J. G., "The Mechanism of Photochemical Smog Formation," *Adv. Environ. Sci. Technol.* 4, 1-262 (1974)
 J. M. Pitts, Jr., and R. L. Metcalf, editors, Wiley-Interscience
 R. F. Hampson
 May 1978

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Temp. Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncert. Factor at 298K, notes |
|------|--|------------------|---|----------------------------------|
| 4.27 | O ₂ + SO ₂ → O + SO ₂ (r) | | ΔH (298) = - 53 kJ/mol | |
| 1.28 | O + SO ₂ → O ₂ + SO (r) | | | |
| | CODATA (1979) eval | | | |
| | Hosann, Krome, Wagner (1968) | 300-1000 | k ₁ = 6 x 10 ⁻¹³ exp(-(3300±500)/T) | 3 |
| | Baulch, et al (1976) review | 580-1145 | k ₁ = 5.8 x 10 ⁻¹³ exp(-3270/T) | |
| | | 440-2100 | k ₁ = 7.5 x 10 ⁻¹³ exp(-3250/T) | |
| | | 440-2100 | k _r = k ₁ /K _{eq} = 2.1 x 10 ⁻¹⁰ T ^{-0.5} exp(-9980/T) | |
| | Breckenridge, Miller (1972) | 300 | k ₂ < 8 x 10 ⁻¹⁷ | |
| | Schofield (1973) review | 400-2500 | k ₁ = 3.0 x 10 ⁻¹³ exp(-2800/T) | |

Recommendation is based largely on the results reported by Hosann, Krome and Wagner (1968) with increased error limits. See the review of Baulch, et al (1976)

REFERENCES

- Baulch, D. L., Drysdale, D. D., Duxbury, J., and Grant, S. J., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 3: Homogeneous Gas Phase Reactions of the O₂-O₃ System, the CO-O₂-H₂ System, and of Sulphur-Containing Species," (Butterworths, London, 1976)
- Breckenridge, W. H., and Miller, T. A., "Kinetic Study by EPR of the Production and Decay of SO(1Δ) in the Reaction of O₂(1Δ_g) with SO(3Σ⁻)," J. Chem. Phys. **56**, 465-474 (1972)
- CODATA(1979). Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.
- Hosann, K., Krome, G., and Wagner, H. Gg., "Schwefelkohlenstoff-Oxydation, Geschwindigkeit von Elementarreaktionen. Teil I," Ber. Bunsenges. Phys. Chem. **72**, 998-1004 (1968)
- Schofield, K., "Evaluated Chemical Kinetic Rate Constants for Various Gas Phase Reactions," J. Phys. Chem. Ref. Data **2**, 25-84 (1973)

P. F. Hampson
 June 1979

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Uncert Factor
at 298K, notes

Reaction/Reference
Temp
Range/K
Reaction Rate Constant
k/cm³molecule⁻¹s⁻¹

No

4.31 O₂ + HS → S6 + Hd
CODATA (1979) eval
Cupitt, Glass (1975)
ΔH (298) = -101 kJ/mol
no recommendation
< 10⁻¹³

295

No recommendation

REFERENCES

- CODATA(1979). Recommendations of the CODATA Task Group on Chemical Kinetics To be published in the Journal of Physical and Chemical Reference Data.
- Cupitt, L. T., and Glass, G. P., "Reactions of SH with Atomic Oxygen and Hydrogen," *Int J. Chem. Kinet.*, Symp. No. 1, 39-50 (1975)
- B. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No | Reaction/Reference | Temp. Range/K | Reaction Rate Constant $k/\text{cm}^6\text{molecule}^{-2}\text{s}^{-1}$ | Uncert Factor at 298K, notes |
|-------|---|------------------|--|---------------------------------|
| 4.35M | $\text{O}_2 + \text{Cl} + \text{M} \rightarrow \text{ClO} + \text{M}$ (f) | | $\Delta H(298) = -32 \text{ kJ/mol}$ | |
| 37. W | $\text{ClO} + \text{M} \rightarrow \text{Cl} + \text{O}_2 + \text{M}$ (r) | | $k_f = (2.0 \pm 0.1) \times 10^{-33} (T/300)^{-1.3}$ | |
| | NASA (1979) eval | 200-300 | $k_f = 2.7 \times 10^{-9} \exp(-(2650 \pm 800)/T) \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1}$ | 7 (a) |
| | | | (a) $k_f = k_f/T_{\text{eq}}$ | |
| | Nicholas, Norrish (1968) | 293 | $k_f = 1.7 \times 10^{-33}$ | |
| | Clyne and Coxon (1968) | 300 | $k_f < 5.5 \times 10^{-33}$ | |
| | Stedman (1968) | 200-300 | $k_f = 5.5 \times 10^{-34}$ | (b) |
| | | | (b) As quoted by Clyne and Coxon (1968). | |

REFERENCES

- Clyne, M. A. A., and Coxon, J. A., "Kinetics Studies of Oxyhalogen Radical Systems," Proc. Roy. Soc., (London) A **302**, 207-231 (1968)
- NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future,"
- Mc D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the June 1979 Harpers Ferry Workshop).
- Nicholas, J. E., and Norrish, R. G. W., "Some Reactions in the Chlorine and Oxygen System Studied by Flash Photolysis," Proc. Roy. Soc. (London) A **307**, 391-397 (1968)
- E. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Temp. Range/K | Reaction Rate Constant k/cm ³ molecule ⁻² s ⁻¹ | Uncertainty Factor at 258K, notes |
|-------|--|------------------|--|--------------------------------------|
| 4.35F | O ₂ + F + M → FO ₂ + M | | ΔH (298) = - 25 kJ/mol | |
| | NASA (1979) eval | 240-300 | k = (1.190.3) × 10 ⁻³² (T/300) ^{-1.741} , M = N ₂ | |
| | CODATA (1979) eval | 270-360 | k = 1.1 × 10 ⁻³² (T/300) ⁻² , M = N ₂ | |
| | Zeitsch (1973) | 270-360 | k _∞ = 3 × 10 ⁻¹¹ cm ³ molecule ⁻¹ s ⁻¹ | 2 |
| | Arutyunov, et al (1976) | 253 | k = 5.2 × 10 ⁻³⁴ exp(656/T), M = He | 3 |
| | Chen, et al (1977) | 252 | k = 7 × 10 ⁻²³ , M = He Rel. M eff: He(1.0), N ₂ (2.4), Ar(0.5) k = 5.4 × 10 ⁻³³ , M = He Rel. M eff: He(1.0), O ₂ (2.8), Ar(1.6) | |

REFERENCES

- Arutyunov, V. S., Popov, L. S., and Chalkin, A. M., "Measurement of the Rate Constant for the Reaction of Fluorine Atoms with Oxygen," *Kinet. and Catal.* **17**, 251-255 (1976)
Trans. of Kinet. & Catal. **17**, 286-291 (1976)
- Chen, B.-L., Treimer, D. W., Center, R. E., and Fyfe, W. I., "A Flash Photolysis, Infrared Chemiluminescence Study of the Rate Constant for the Recombination Reaction F + O₂ + M," *J. Chem. Phys.* **66**, 5513-5519 (1977)
- CODATA(1979), Recommendations of the CODATA Task Group on Chemical Kinetics, to be published in the *Journal of Physical and Chemical Reference Data*.
- NASA (1979), Recommendations of the NASA Panel for Data Evaluation, published in NASA SP 1049 "The Stratosphere: Present and Future," B. D. Hudson and E. I. Reed, Editors, Dec. 1975 (report of the June 1975 Harper Ferry Workshop).
- Zeitsch, C., "Some Combination Reactions of Fluorine Atoms," *Combustion Institute European Symp.*, P. J. Wainter, ed., No. 35, Academic Press, London (1973)
- B. F. Hampson
 June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No | Reaction/Reference | Temp. Range/K | Reaction Rate Constant $\text{M/cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | Uncert Factor at 298K, notes |
|-------|--|------------------|--|---------------------------------|
| 4.46a | $\text{O}_2 + \text{CN} \rightarrow \text{NCO} + \text{O}$ Albers, et al (1975) | 275-398 | $\Delta H (298) = -27 \text{ kJ/mol}$ $5.3 \times 10^{-11} \exp(-500470/T)$ | 1-3 |

These results are in agreement with earlier work for room temperature value but not for temperature dependence

REFERENCES

Albers, E. A., Hoyermann, E., Schacke, E., Schmetjko, E. J., Wagner, H. Gg.,
and Wolfrum, J., "Absolute Rate Coefficients for the Reaction of H-Atoms
with N_2O and Some Reactions of CN Radicals," Symp. Combust. 15th
(Combustion Institute, Pittsburgh, 1975) 765-773

E. F. Hampson
May 1976

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No | Reaction/Reference | Temp- Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncert Factor at 298K, notes |
|------|--|------------------|--|---------------------------------|
| 4.47 | O ₂ + C ₂ H ₆ → C ₂ H ₅ + HO ₂ | | ΔH (298) = -146 kJ/mol | |
| | NASA (1979) eval | 200-300 | 5 x 10 ⁻¹² exp((0±250)/T) | 1-4 |
| | CODATA (1979) eval | 298 | 5.1 x 10 ⁻¹² | 1-25 |
| | Shibuya, et al (1977) | 300 | (5.6±0.9) x 10 ⁻¹² | |
| | Clark, et al (1978) | 300 | (4.0±0.8) x 10 ⁻¹² | |
| | Washida, et al (1974) | 297 | (5.7±1.2) x 10 ⁻¹² | |
| | Peeters, Mahnen (1973) | 1400-1800 | 5 x 10 ⁻¹¹ | |

The value for k (298 K) is the average of the determinations by Washida et al (1974), Shibuya et al (1977) and Clark et al (1978). Inclusion of the latter two measurements results in a value lower than that recommended in NASA 1010

REFERENCES

- Clark, J. E., Moore, C. B., and Reilly, J. P., "HCO Radical Kinetics: Conjunction of Laser Photolysis and Intracavity Dye Laser Spectroscopy," *Int. J. Chem. Kinet.* **10**, 427-431 (1978a)
- CODATA(1979). Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the *Journal of Physical and Chemical Reference Data*.
- NASA RP-1010. "Chlorofluoromethanes and the Stratosphere" E. D. Hudson, Editor, August 1977 This reference contains the NASA (1977) rate constant recommendations.
- NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," E. D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the June 1979 Harpers Ferry Workshop).
- Peeters, J., and Mahnen, G., "Reaction Mechanisms and Rate Constants of Elementary Steps in Methane-Oxygen Flames," *Symp. Combust.* **14th** (Combustion Institute, Pittsburgh, 1973) 133-141

Shibuya, K., Ebata, T., Ohi, K., and Tanaka, I., "Rate Constant Measurements for the Reactions of HCO with NO and O₂ in the Gas Phase," *J. Phys. Chem.*, **81**, 2292-2294 (1977)

Washida, M., Martinez, M. I., and Bayes, K. D., "The Oxidation of Peraryl Radicals," *Z. Naturforsch.*, **A 29**, 251-255 (1974)

R. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No | Reaction/Reference | Temp. Range/K | Reaction Rate Constant $k/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$ | Uncert Factor at 298K, notes |
|------|--|------------------|---|---------------------------------|
| 4.49 | $\text{O}_2 + \text{CH}_3 \rightarrow \text{CH}_2\text{O} + \text{H}\cdot$ C6DATA (1979) eval Washida, Bayes (1976) Basco, et al (1972) | 259-341 295 | $\Delta H (298) = -215 \text{ kJ/mol}$ No recommendation $2.9 \times 10^{-13} \exp(-940/T)$ $\pm 3 \times 10^{-16}$ a. Based on negative result and sensitivity limit, other measurements at higher T suggest an appreciable activation energy. | estimated (a) |

No recommendation

REFERENCES

- Basco, N., James, D. G. L., and James, F. G., "A Quantitative Study of Alkyl Radical Reactions by Kinetic Spectroscopy. II. Combination of the Methyl Radical with the Oxygen Molecule," *Int. J. Chem. Kinet.* **4**, 129-149 (1972)
- C6DATA(1979), Recommendations of the C6DATA Task Group on Chemical Kinetics. To be published in the *Journal of Physical and Chemical Reference Data*.
- Washida, N., and Bayes, E. D., "The Reactions of Methyl Radicals with Atomic and Molecular Oxygen," *Int. J. Chem. Kinet.* **8**, 777-794 (1976)
- R. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No | Reaction/Reference | Temp. Range/K | Reaction Rate Constant $k/\text{cm}^6\text{molecule}^{-2}\text{s}^{-1}$ | Uncert Factor at 298K, notes |
|-------|--|------------------|---|---------------------------------|
| | | | | |
| 4.49N | $\text{O}_2 + \text{CH}_3 + \text{M} \rightarrow \text{CH}_3\text{O}_2 + \text{M}$ NASA (1979) eval | 200-300 | $\Delta H (298) = -135 \text{ kJ/mol}$ $k = (2.2 \pm 1.1) \times 10^{-31} (T/300)^{-2.2 \pm 1.0}$, $\text{M} = \text{N}_2$ $k_{\infty} = (2.0 \pm 1.0) \times 10^{-12} (T/300)^{-1.7 \pm 1.0}$ | (b) 2 |
| | CODATA (1979) eval | 260-340 | $k = 2.6 \times 10^{-31} (T/300)^{-3}$, $\text{M} = \text{N}_2$ | 2(b) |
| | Parkes (1977) | 200-400 | $k_{\infty} = 2 \times 10^{-12}$ | |
| | | 298 | $k = 3.1 \times 10^{-31}$, $\text{M} = \text{N}_2$ | |
| | | | $k_{\infty} = 1.2 \times 10^{-12}$ | (b) |
| | Laufer, Bass (1975) | 298 | $10^{12} \frac{k_{\text{rel}}}{k_{\text{rel}}}$ $\frac{P(\text{N}_2)/\text{atm}}{50}$ | (a) |
| | | | 0.45 0.7 1.2 1.7 | |
| | Washida, Bayes (1976) | 300 | 5.0×10^{-13} 1.5×10^{-31} $\text{M} = \text{N}_2$ | (b) (b) |
| | Bochanadel, et al (1977) | 295 | 2.2×10^{-12} | (b) |
| | Basco, et al (1972) | 295 | 5.1×10^{-13} | (b) |
| | | | 2.6×10^{-31} $\text{M} = \text{N}_2$ | |
| | van den Bergh, Callear (1971) | 295 | 1.6×10^{-12} 6×10^{-31} $\text{M} = \text{C}_2\text{H}_2$ | preliminary preliminary |
| | | | (a) Values are based on $k(\text{CH}_3 + \text{CH}_3) =$ 9.5×10^{-11} , given in Bass, Laufer (1973). | |
| | | | (b) 2nd order high pressure limit in $\text{cm}^6\text{molecule}^{-1}\text{s}^{-1}$ | |

REFERENCES

Basco, M., James, D. G. L., and James, F. Co. "A Quantitative Study of Alkyl Radical Reactions by Kinetic Spectroscopy. II. Combination of the Methyl Radical with the Oxygen Molecule," *Int. J. Chem. Kinetic* **4**, 129-145 (1972)

CODATA(1979): Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the *Journal of Physical and Chemical Reference Data*.

Bochanadel, C. J., Chornley, J. A., Boyle, J. W., and Ogren, P. J., "Absorption Spectrum and Rates of Formation and Decay of the CH_3O_2 Radical," *J. Phys. Chem.* **81**, 3-7 (1977)

Laufer, A. H., and Bass, A. M., "Rate Constants of the Combination of Methyl Radicals with Nitric Oxide and Oxygen," *Int. J. Chem. Kinetic* **7**, 639-642 (1975)

- NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," R. D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the June 1979 Harpers Ferry Workshop).
- Parkes, D. A., "Oxidation of Methyl Radicals at Room Temperature," *Int. J. Chem. Kinet.*, **9**, 451-465 (1977)
- van den Bergh, E. E., and Callear, A. D., "Spectroscopic Measurement of the Rate of the Gas-Phase Combination of Methyl Radicals with Nitric Oxide and Oxygen at 295 K," *Trans. Faraday Soc.*, **67**, 2017-2024 (1971)
- Vashide, N., and Beyer, E. D., "The Reactions of Methyl Radicals with Atomic and Molecular Oxygen," *Int. J. Chem. Kinet.*, **8**, 777-794 (1976)
- E. F. Naspaoen
June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No | Reaction/Reference | Temp. Range/K | Reaction Rate Constant $k/\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ | Uncert. Factor at 298K, notes |
|------|---|------------------|--|----------------------------------|
| 5. M | $\text{O}_2(^1\text{A}) + \text{M} \rightarrow \text{O}_2 + \text{M}$ | | $\Delta H (298) = -94 \text{ kJ/mol}$ | |
| | Hampson, et al (1973) review | 285-322 | $2.2 \times 10^{-18} (T/300)^{0.8} \text{ M} = \text{O}_2$ | 1.3 |
| | Buenos, et al (1974) | 77 | $1.1 \times 10^{-18} \text{ M} = \text{O}_2$ (a) Liquid phase, when combined with gas phase data of Findlay and Snelling (1971a) (summarized in Hampson, et al (1973) | (a) |
| | Hampson, et al (1973) review | 300 | $k = 2.2 \times 10^{-18} (T/300)^{0.5}$ $< 2 \times 10^{-20} \text{ M} = \text{N}_2$ | |
| | Collins, et al (1973) | 300 | $1.4 \times 10^{-19} \text{ M} = \text{N}_2$ | |
| | Penzhorn, et al (1974) | 300 | $3.9 \times 10^{-20} \text{ M} = \text{SO}_2$ | |
| | Penzhorn, et al (1975) | 300 | $2.1 \times 10^{-19} \text{ M} = \text{H}_2\text{S}$ | |
| | | 300 | $k = 10^{-18} \text{ M}$ 0.4 CF_2Cl_2 0.08 CCl_4 1.01 CH_3Cl 0.87 CH_2Cl_2 0.92 CHCl_3 | |
| | Fisher, McCarty (1966) | 300 | $< 3 \times 10^{-16} \text{ M} = \text{C}_4$ (b) total rate, quenching and reaction | (b) |

For $\text{M} = \text{O}_2$ and N_2 use the recommendations in the review of Hampson, et al (1973). For sulfur compounds and for halocarbons use the values reported by Penzhorn et al (1974) and (1975) respectively

REFERENCES

- Collins, R. J., Husain, D., and Donovan, R. J., "Kinetic and Spectroscopic Studies of $\text{O}_2(^1\text{A}_g)$ by Time-Resolved Absorption Spectroscopy in the Vacuum Ultra-violet," *J. Chem. Soc., Faraday Trans. II* **69**, 145-157 (1973)
- Findlay, R. D., and Snelling, D. R., "Collisional Deactivation of $\text{O}_2(^1\text{A}_g)$," *J. Chem. Phys.* **55**, 545-551 (1971a)
- Fisher, R. E., and McCarty, M. J., "Study of the Reaction of Electronically Excited Oxygen Molecules with Carbon Monoxide," *J. Chem. Phys.* **45**, 781-784 (1966)
- Hampson, R. F., (editor), "Survey of Photochemical and Rate Data for Twenty-Eight Reactions of Interest in Atmospheric Chemistry," *J. Phys. Chem. Ref. Data* **2**, No. 2 pgs. 267-312 (1973). These are revised versions of data sheets originally distributed as NBS Reports 10692 and 10828.

Buesfle, D. L., Black, G., Edelstein, S. A., and Sharpless, R. L., "Fluorescence and Quenching of $O_2(^1A_g)$ and $[O_2(^1A_g)]_2$ in Liquid Oxygen," J. Chem. Phys. **59**, 4471-4474 (1974)

Penzhorn, R-D., Gusten, E., Schurath, U., and Becker, K. H., "Quenching of Singlet Molecular Oxygen by Some Atmospheric Pollutants," Environ. Sci. Technol. **8**, 907 (1974)

Penzhorn, R-D., Gusten, E., Schurath, U., and Becker, K. H., "Halogenierte Kohlenwasserstoffe in der Atmosphäre: Geschwindigkeitskonstanten für die Löschung von Metastabilen Sauerstoffmolekülen," Staub - Reinhalt Luft **35**, 95-98 (1975)

R. F. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No | Reaction/Reference | Temp- Range/K | Reaction Rate Constant $\text{m}^3/\text{mole} \cdot \text{s}^{-1}$ | Uncert. Factor at 298K, notes |
|-----|---|------------------|--|----------------------------------|
| 5.7 | $\text{O}_2(^1\text{A}) + \text{O}_3 \rightarrow 2\text{O}_2 + \text{O}$ This survey | | $\Delta H (298) = 12 \text{ kJ/mol}$ | 1-2 |
| | Clark, Jones, Wayne (1970) | 200-350 | $1.2 \times 10^{-11} \exp(-2400/T)$ | |
| | Findlay, Smelling (1971) | 195-439 | $6.6 \times 10^{-13} \exp(-1560/T)$ | |
| | Becker, et al (1972) | 283-321 | $4.5 \times 10^{-11} \exp(-2830/T)$ | |
| | Collins, et al (1973) | 296-360 | $6.0 \times 10^{-11} \exp(-2850/T)$ | |
| | Schofield (1972) review | 300 | 4.4×10^{-15} | |
| | | 283-321 | $4.5 \times 10^{-11} \exp(-2830/T)$ | |

This evaluation recommends a room temperature value which is the average of the four reported values. The temperature dependence is taken as the average of the reported values, and the pre-exponential factor derived to fit the room temperature value

REFERENCES

- Becker, K. E., Groth, W., and Schurath, U., "Reactions of $\text{O}_2(^1\text{A}_g)$ with Ozone," *Chem. Phys. Lett.* **14**, 489-492 (1972)
- Clark, I., Do., Jones, I. T. M., and Wayne, R. P., "The Kinetics of the Reaction between $\text{O}_2(^1\text{A}_g)$ and Ozone," *Proc. Roy. Soc. London A* **317**, 407-416 (1970)
- Collins, R. J., Husain, D., and Donovan, R. J., "Kinetic and Spectroscopic Studies of $\text{O}_2(^1\text{A}_g)$ by Time-Resolved Absorption Spectroscopy in the Vacuum Ultra-violet," *J. Chem. Soc., Faraday Trans. II* **69**, 145-157 (1973)
- Findlay, R. D., and Smelling, D. R., "Temperature Dependence of the Rate Constant for the Reaction $\text{O}_2(^1\text{A}_g) + \text{O}_3 \rightarrow 2\text{O}_2 + \text{O}$," *J. Chem. Phys.* **54**, 2750-2755 (1971)
- Schofield, K., "The Rate of Destruction of $\text{O}_2(^1\text{A}_g)$ by Atomic Hydrogen," *Intern. J. Chem. Kinet.* **4**, 255-263 (1972)

R. F. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No | Reaction/Reference | Temp. Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncert Factor at 298K, notes |
|-----|---|---------------------------|--|---------------------------------|
| 5.6 | $O_2(^1\Delta) + N \rightarrow NO + O$ Schmidt, Schiff (1973) Westenberg, et al (1970) Clark, Wayne (1970) | 300 195-300 195-431 | $\Delta H (298) = -226 \text{ kJ/mol}$ $k < k(N + O_2 \rightarrow NO + O)$ $k < k(N + O_2 \rightarrow NO + O)$ $k = 2 \times 10^{-14} \exp(-600/T)$ (a) probably refers to physical deactivation, not chemical reaction; see above refs | probably (a) |

No recommendation

REFERENCES

- Clark, I. D., and Wayne, R. P., "Kinetics of the Reaction between Atomic Nitrogen and Molecular Oxygen in the Ground ($^3\Sigma_g^-$) and First Excited ($^1\Delta_g$) States," Proc. Roy. Soc. London A **316**, 539-550 (1970)
- Westenberg, A. A., Roscoe, J. O., and DeHaas, N., "Rate Measurements on $N + O_2(^1\Delta_g) \rightarrow NO + O$ and $N + O_2(^1\Delta_g) \rightarrow OH + O$," Chem. Phys. Lett. **7**, 597-599 (1970)
- Schmidt, C., and Schiff, H. I., "Reactions of $O_2(^1\Delta_g)$ with Atomic Nitrogen and Hydrogen," Chem. Phys. Lett. **23**, 339-342 (1973)
- R. P. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Uncert Factor
at 298K, notes

Reaction/Reference

Temp.
Range/K

Reaction Rate Constant
k/cm³molecule⁻¹s⁻¹

No

| | | | | | |
|-----|---|-----|-------------------------------|-------------------------------------|-----|
| 5.9 | $O_2(^1\Delta) + NO \rightarrow NO_2 + NO(v=4)$ | 300 | 4.5×10^{-17} | $\Delta H(298) = -6 \text{ kJ/mol}$ | 1.4 |
| | Becker, et al (1971) | 300 | 2.5×10^{-17} | | |
| | Yaron, et al (1976) | 293 | $(4.5 \pm 1) \times 10^{-17}$ | | |
| | Glachard, et al (1976) | 300 | $NO(v=4) \text{ observed}$ | | |
| | Goryzlo, Thrush (1973) | | | | |

This evaluation selects the value reported by Becker, et al (1971). It is confirmed by the results of Glachard, et al (1976). Goryzlo and Thrush concluded that all the observed NO excitation is due to the indicated process followed by vibrational relaxation

REFERENCES

- Becker, E. H., Groth, W., and Schurath, U., "The Quenching of Metastable $O_2(^1\Delta)$ and $O_2(^1\Sigma_g^-)$ Molecules," *Chem. Phys. Lett.* **8**, 259-262 (1971)
- Glachard, D. J., Harris, G. W., and Wayne, R. P., "Energy Transfer from Excited NO_2 to Molecular Oxygen," *J. Chem. Soc., Faraday Trans. II* **72**, 619-630 (1976)
- Goryzlo, E. A., and Thrush, B. A., "Vibrational Excitation of NO in its Collisional Quenching of $O_2(^1\Delta_g)$," *Chem. Phys. Lett.* **23**, 34-36 (1973)
- Yaron, M., von Engel, A., and Vidaud, P. M., "The Collisional Quenching of $O_2(^1\Delta_g)$ by NO and CO_2 ," *Chem. Phys. Lett.* **37**, 159-161 (1976)
- R. F. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Uncert. Factor
at 298K, notes

Reaction Rate Constant
 $\text{L}/\text{cm}^3\text{-molecule}^{-1}\text{s}^{-1}$

Temp.
Range/K

Reaction/Reference

No

(a)

5.18 $\text{O}_2(^1\text{A}) + \text{H} \rightarrow \text{products}$
Schmidt, Schiff (1973)

$(2.5 \pm 0.5) \times 10^{-14}$

(a) expt could not distinguish between
chemical rxn and physical quenching

rxn to give $\text{HO} + \text{O}$ as products not observed

Westenberg, et al (1970)

300

300

No recommendation

REFERENCES

Schmidt, C., and Schiff, H. Lo., "Reactions of $\text{O}_2(^1\text{A}_g)$ with Atomic Nitrogen
and Hydrogen," *Chem. Phys. Lett.* 23, 339-342 (1973)

Westenberg, A. A., Roscoe, J. W., and DeHaas, M., "Rate Measurements on
 $\text{H} + \text{O}_2(^1\text{A}_g) \rightarrow \text{HO} + \text{O}$ and $\text{H} + \text{O}_2(^1\text{A}_g) \rightarrow \text{OH} + \text{O}$," *Chem. Phys. Lett.* 1,
597-599 (1970)

R. F. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No | Reaction/Reference | Temp- Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncert Factor at 298K, notes |
|------|--|------------------|--|---------------------------------|
| 5.27 | O ₂ (¹ Δ) + SO → SO ₂ + SO(¹ Δ) Breckenridge, Miller (1972) | 300 | ΔH (298) = - 20 kJ/mol 3.5 ± 0.36 × 10 ⁻¹³ | |

No recommendation

REFERENCES

Breckenridge, W. H., and Miller, T. A., "Kinetic Study by EPR of the Production and Decay of SO(¹Δ) in the Reaction of O₂(¹Δ_g) with SO(³Σ⁻).", J. Chem. Phys. **56**, 465-474 (1972)

E. P. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No | Reaction/Reference | Temp. Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncert Factor at 298K, notes |
|-----|---|------------------|--|---------------------------------|
| 6.4 | O ₂ (¹ Σ) + M → O ₂ + M Hampson, et al (1973) review | 300 | ΔH (298) = -157 kJ/mol 1.5 x 10 ⁻¹⁶ , M = O ₂ 2.0 x 10 ⁻¹⁵ , M = N ₂ 4 x 10 ⁻¹² , M = H ₂ O | 1-3 1-3 1-5 |

Use these recommendations from the review of Hampson, et al (1973)

REFERENCES

Hampson, R. F., (editor), "Survey of Photochemical and Rate Data for Twenty-Eight Reactions of Interest in Atmospheric Chemistry," J. Phys. Chem. Ref. Data 2, No. 2 pgs. 267-312 (1973). These are revised versions of data sheets originally distributed as NBS Reports 10692 and 10828.

R. F. Hampson
 May 1978

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Uncert. Factor
at 298K, notes

Reaction/Reference Temp.
Range/K Reaction Rate Constant
k/cm³molecule⁻¹s⁻¹

No

| | | |
|-----|--------------------------------|--|
| 7.8 | $O_3 + H \rightarrow HO + O_2$ | $\Delta H (298) = -525 \text{ kJ/mol}$ |
| | NASA (1979) eval | $< 1 \times 10^{-15}$ |
| | CODATA (1979) eval | $< 5 \times 10^{-16}$ |
| | Stief, et al (1979) | $< 5 \times 10^{-16}$ |
| | Phillips, Schiff (1962) | 5.7×10^{-13} |

New recommendation based on results of Stief et al (1979). Note that this is an upper limit based on instrumental sensitivity. NASA RP-1010 recommended an estimated temperature dependent expression based on the room temperature value of Phillips and Schiff (1962) which was about a factor of 500 greater than the upper limit recommended here. Results of Garvin and Broida (1963) cast doubt on the fast rate reported by Phillips and Schiff and as such support Stief's results. Independent confirmation is needed

REFERENCES

CODATA(1979). Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.

Garvin, D., and Broida, R. P., "Atomic Flame Reactions Involving H Atoms, N Atoms and Ozone," Sympo Combust, 2. (Academic Press, New York, 1963) 676-686

NASA RP-1010, "Chlorofluoromethanes and the Stratosphere" R. D. Hudson, Editor, August 1977 This reference contains the NASA (1977) rate constant recommendations.

NASA (1979). Recommendations of the NASA Panel for Data Evaluation to be published in the report of the Stratosphere Workshop, Harpers Ferry, June 1979. These recommendations update those published in W. B. DeMore et al, "Chemical Kinetic and Photochemical Data for use in Stratospheric Modelling" Jet Propulsion Laboratory Publication 79-27, April 15, 1979.

Phillips, L. F., and Schiff, H. I., "Mass Spectrometric Studies of Atom Reactions. I. Reactions in the Atomic Nitrogen-Ozone System," J. Chem. Phys. 36, 1509-1517 (1962)

Stief, L. J., Payne, W. E., Lee, J. E., and Michael, J. W.,
"The Reaction $M(4s) + O_2$: An Upper Limit for the
Rate Constant at 298 K," J. Chem. Phys. **70**, 5241-5243
(1979)

P. F. Hampson
June 1979

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS
CHEMICAL KINETICS DATA SURVEY

| Mo | Reaction/Reference | Temp Range/K | Reaction Rate Constant $k/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$ | ΔH (298) = -200 kJ/mol | Uncert Factor at 298K, notes |
|------|---|-----------------|--|--------------------------------|------------------------------------|
| 7.9 | $\text{O}_3 + \text{NO} \rightarrow \text{NO}_2 + \text{O}_2$ (z) | | | | |
| 8.10 | $\text{O}_2 + \text{NO}_2 \rightarrow \text{NO} + \text{O}_3$ (r) | | | | |
| | NASA (1979) eval | | | | |
| | CODATA (1979) eval | | | | |
| | Birks, et al (1976) | 203-361 | $k_1 = 2.34 \pm 0.23 \times 10^{-12} \exp(-1450 \pm 50/T)$ | | 1 15 |
| | Stedman, Niki (1973) | 298 | $k_1 = 1.73 \pm 0.1 \times 10^{-14}$ | | |
| | Baulch, et al (1973) review | 200-350 | $k_1 = 1.5 \times 10^{-12} \exp(-1330/T)$ | | |
| | Ghormley, et al (1973) | 298 | $k_1 = k_1/K_{\text{eq}} = 2.8 \times 10^{-12} \exp(-25400/T)$ | | |
| | Bemand, et al (1974) | 300 | $k_1 = 1.41 \times 10^{-14}$ | | |
| | Becker, Schurath, Seitz (1974) | 290 | $k_1 = 1.81 \pm 0.13 \times 10^{-14}$ | | |
| | | | $k_1 = 1.70 \times 10^{-14}$ | | |

Recommended Arrhenius expression is that of Birks et al (1976). Room temperature value is an average of Birks et al (1976), Bemand et al (1974), Becker et al (1974) and Stedman and Niki (1973). The slightly lower pre-exponential factor recommended in NASA RP-1010 was based on an alternative analysis of the primary data in Birks et al and inclusion of older room temperature data. The present recommendation accepts the data analysis given in Birks' paper. Independent confirmation of the temperature dependence is needed.

PREFERENCES

- Baulch, D. L., Drysdale, D. D., and Horne, D. G., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 2: Homogeneous Gas Phase Reactions of the H_2 - N_2 - O_2 System," (Butterworths, London, 1973)
- Becker, K. H., Schurath, U., and Seltz, W., "Ozone-Olefin Reactions in the Gas Phase: 1. Rate Constants and Activation Energies," *Int. J. Chem. Kinet.* **6**, 725-739 (1974)
- Bemand, P. P., Clyne, M. A., and Watson, R. T., "Atomic Resonance Fluorescence and Mass Spectrometry for Measurements of the Rate Constants for Elementary Reactions: $G(P_j) + NO_2 \rightarrow NO + O_2$ and $NO + O_3 \rightarrow NO_2 + O_2$," *J. Chem. Soc., Faraday Trans. II* **70**, 564-576 (1974)
- Birks, J. W., Shoemaker, E., Leck, T. J., and Hinton, D. M., "Studies of Reactions of Importance in the Stratosphere: 1. Reaction of Nitric Oxide with Ozone," *J. Chem. Phys.* **65**, 5181-5185 (1976)
- CODATA(1979). Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.

Ghermley, J. A., Ellsworth, E. L., and Mehanadel, C. J., "Reaction of Excited Oxygen Atoms with Nitrous Oxide, Rate Constants for Reaction of Ozone with Nitric Oxide and with Nitrogen Dioxide," J. Phys. Chem. **77**, 1341-1345 (1973). Erratum: **78**, 2698 (1974)

NASA RP-1010, "Chlorofluoromethanes and the Stratosphere" E. D. Hudson, Editor, August 1977 This reference contains the NASA (1977) rate constant recommendations.

NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," E. D. Hudson and E. L. Reed, Editors, Deco 1979 (report of the June 1979 Harpers Perry Workshop).

Photochemical Data for use in Stratospheric Modelling" Jet Propulsion Laboratory Publication 79-27, April 15, 1979.

Stedman, D. E., and Miki, E., "Kinetics and Mechanism for the Photolysis of Nitrogen Dioxide in Air," J. Phys. Chem. **77**, 2604-2609 (1973)

E. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Uncert. Factor
at 298K, notes

Reaction/Reference

Temp.
Range/K

Reaction Rate Constant
k/cm³molecule⁻¹s⁻¹

No

| | | | | |
|-----|---|-------------------------------|---|--|
| 7.9 | $\phi_3 \cdot \text{NO} \rightarrow \text{NO}_2$ ($2\phi_{1,2}$) $\cdot \phi_2$ (1) - NO_2 ($2\phi_{1,2}$) $\cdot \phi_2$ (2) - $\phi_3 \cdot \text{NO}$ (3) | 153-373 158-437 138-410 | see discussion see discussion $k_1 = 1.0 \times 10^{-12} \exp(-1450/T)$ $k_2 = 3.6 \times 10^{-13} \exp(-520/T)$ $k_3 = 1.1 \times 10^{-13}$ at 333 K and at 143 K with minimum value of 0.62×10^{-13} at approx 230K | |
|-----|---|-------------------------------|---|--|

Measured quantity in all studies is $(k_1 \cdot k_2 \cdot k_3)$.
Values of this quantity measured by Kurylo et al and by
Hui, Cool are in good agreement; values reported by
Bar-Ziv, Moy and Gordon are systematically higher
below 300K.

Hui and Cool derived values as a function of temperature
for k_1 , k_2 , and k_3 given above from an analysis of
the temperature dependent data for $(k_1 \cdot k_2 \cdot k_3)$ reported
by the three groups, the temperature dependence of the
enhancement factor for rxn channel (1) reported by Moy,
Bar-Ziv and Gordon (1977), their own temperature dependent
data for the ratio of the enhancement factors for rxn
channels (1) and (2) and the rate constant for channels
(1) and (2) for thermal ozone reported by Clough and
Thrush (1967)

REFERENCES

- Bar-Ziv, E., Moy, J., and Gordon, R. J., "Temperature Dependence of the Laser Enhanced Reaction $\text{NO} + \text{O}_3(001) \rightarrow \text{O}_2 + \text{O}_2$ Contribution from Reactive and Non-Reactive Channels," *J. Chem. Phys.* **68**, 1013 (1978)
- Clough, P. M., and Thrush, B. A., "Mechanism of Chemiluminescent Reaction between Nitric Oxide and Ozone," *Trans. Faraday Soc.* **63**, 915-925 (1967)
- Hui, E.-K., and Cool, T. A., "Experiments Concerning the Laser Enhanced Reaction Between Vibrationally Excited O_3 and NO ," *J. Chem. Phys.* **68**, 1022-1037 (1978)
- Kurylo, M. J., Braun, W., and Xuan, C. H., "Infrared Laser Enhanced Reactions: Temperature Resolution of the Chemical Dynamics of the $\text{O}_3 + \text{NO}$ Reaction System," *J. Chem. Phys.* **62**, 2065-2071 (1975)
- Moy, J., Bar-Ziv, E., and Gordon, R. J., "Temperature Dependence of the Laser Enhanced Reaction $\text{NO} + \text{O}_3(001) \rightarrow \text{NO}_2(\text{ }^2\text{B}_1, 2) + \text{O}_2$," *J. Chem. Phys.* **66**, 5439-5446 (1977)

P. F. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No | Reaction/Reference | Temp. Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncert. Factor at 298K, notes |
|------|---|---------------|--|----------------------------------|
| 7.10 | O ₃ + NO ₂ → NO ₃ + O ₂ (2) | | | |
| 4.11 | O ₂ + NO ₃ → O ₃ + NO ₂ (r) | | | |
| | NASA (1979) eval | | | |
| | CODATA (1979) eval | | | |
| | Davis, Prusaczyk, Dwyer, Kim (1974) | 200-300 | k ₁ = 1.2 x 10 ⁻¹³ exp(-(2450±140)/T) | 1.15 |
| | Graham, Johnston (1974) | 230-360 | k ₁ = 1.2 x 10 ⁻¹³ exp(-(2450±150)/T) | 1.15 |
| | Hule, Herron (1974a) | 240-343 | k ₁ = 9.76 ± 0.54 x 10 ⁻¹⁴ exp(-2427 ± 140/T) | |
| | Baulch, et al (1973) review | 231-298 | k ₁ = 1.34 ± 0.11 x 10 ⁻¹³ exp(-2466 ± 30/T) | |
| | Wu, Morris, Niki (1973) | 259-362 | k ₁ = 1.57 ± 0.41 x 10 ⁻¹³ exp(-2509 ± 76/T) | |
| | Chornley, et al (1973) | 300 | k ₁ = 7 x 10 ⁻³⁴ based on k ₁ | |
| | Stedman, Niki (1973) | 299 | k ₁ = 4.4 x 10 ⁻¹⁷ | |
| | Becker, Schurath, Seltz (1974) | 298 | k ₁ = 3.2 x 10 ⁻¹⁷ | |
| | | 298 | k ₁ = 6.5 ± 0.8 x 10 ⁻¹⁷ | |
| | | 289 | k ₁ = 3.24 x 10 ⁻¹⁷ | |

Based on least squares fit to data in studies of Davis et al (1974), Graham and Johnston (1974) and Hule and Herron (1974a)

REFERENCES

- Baulch, D. L., Drysdale, D. D., and Horne, D. G., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 2: Homogeneous Gas Phase Reactions of the H₂-N₂-O₂ System," (Butterworths, London, 1973)
- Becker, K. E., Schurath, U., and Seltz, E., "Ozone-Olefin Reactions in the Gas Phase. I. Rate Constants and Activation Energies," *Int. J. Chem. Kinet.* **5**, 725-739 (1974)
- Davis, D. D., Prusaczyk, J., Dwyer, M., and Kim, P., "A Stop-Flow Time of Flight Mass Spectrometry Kinetics Study, Reaction of Ozone with Nitrogen Dioxide and Sulfur Dioxide," *J. Phys. Chem.* **78**, 1775-1779 (1974)
- Chornley, J. A., Ellsworth, R. L., and Hochanadel, C. J., "Reaction of Excited Oxygen Atoms with Nitrous Oxide, Rate Constants for Reaction of Ozone with Nitric Oxide and with Nitrogen Dioxide," *J. Phys. Chem.* **77**, 1341-1345 (1973). Erratum: **78**, 2698 (1974)

- Graham, R. A., and Johnston, R. A., "Kinetics of the Gas-Phase Reaction between Ozone and Nitrogen Dioxide," *J. Chem. Phys.*, **58**, 4628-4629 (1974)
- Hale, B. E., and Morron, J. T., "The Rate Constant for the Reaction $O_3 + NO_2 \rightarrow O_2 + NO_3$ Over the Temperature Range 259-362° K," *Chem. Phys. Lett.*, **27**, 411-416 (1974a)
- NASA (1979), Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future."
- R. D. Hudson and R. J. Reed, Editors, Dec. 1979 (report of the June 1979 Harpers Ferry Workshop).
- Stedman, D. E., and Niki, E., "Kinetics and Mechanism for the Photolysis of Nitrogen Dioxide in Air," *J. Phys. Chem.*, **77**, 2604-2609 (1973)
- Wu, C. E., Morris, E. D., Jr., and Niki, E., "The Reaction of Nitrogen Dioxide with Ozone," *J. Phys. Chem.*, **77**, 2507-2511 (1973)
- R. P. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No | Reaction/Reference | Temp. Range/K | Reaction Rate Constant $k/\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ | Uncert. Factor at 298K, notes |
|------|---|------------------|--|----------------------------------|
| 7.14 | $\text{C}_3 + \text{H} \rightarrow \text{H}_2 + \text{C}_2$ | | $\Delta H (298) = -322 \text{ kJ/mol}$ | |
| | NASA (1979) eval | 200-300 | $1.4 \times 10^{-10} \exp(-(470 \pm 200)/T)$ | 1.25 |
| | CODATA (1979) eval | 220-360 | $1.4 \times 10^{-10} \exp(-(480 \pm 100)/T)$ | 1.5 |
| | Keyser (1979a) | 190-424 | $(1.5 \pm 0.2) \times 10^{-10} \exp(-(499 \pm 32)/T)$ | |
| | Lee, et al (1978b) | 219-360 | $(1.3 \pm 0.3) \times 10^{-10} \exp(-(449 \pm 58)/T)$ | |
| | Clyne, Monkhous (1977) | 298-638 | $(1.0 \pm 0.2) \times 10^{-10} \exp(-(516 \pm 60)/T)$ | |
| | Phillips, Schiff (1962) | 300 | $2.6 \pm 0.5 \times 10^{-11}$ | |

This recommendation is an average of the recent results of Lee et al (1978b) and Keyser (1979a), which are in excellent agreement over the 200-400 K range. An earlier study by Clyne and Monkhous (1977) is in very good agreement on the T dependence in the range 300-650 K but lies about 60% below the recommended values. Although we have no reason not to believe the Clyne and Monkhous values, we prefer the two studies that are in excellent agreement, especially since they were carried out over the T range of interest.

Recent results by Finlayson-Pitts and Kleindienst (1979) agree well with the present recommendation although they do indicate a second reaction channel to give $\text{H}_2 + \text{C}$ (~ 25%). Confirmation is needed

REFERENCES

Clyne, M. A., and Monkhous, P. B., "Atomic Resonance Fluorescence for Rate Constants of Rapid Bimolecular Reactions. Part 5-Hydrogen Atom Reactions; $\text{H} + \text{H}_2$ and $\text{H} + \text{C}_3$," J. Chem. Soc., Faraday Trans. II **73**, 298-309 (1977)

CODATA(1979). Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.

Finlayson-Pitts, B. J., and Kleindienst, T. B., "The Reaction of Hydrogen Atoms with Ozone: Evidence for a Second Reaction Path Producing H_2 and $\text{C}(^3\text{P})$," J. Chem. Phys. **70**, 4804-4806 (1979)

- Keyer, L. P., "Absolute Rate and Temperature Dependence of
of the Reaction between Hydrogen ($2S$) Atoms and Ozone,"
J. Phys. Chem. **83**, 645-648 (1979a)
- Lee, J. E., Michael, J. V., Payne, W. A., and Stief, L. J., "Absolute Rate
of the Reaction of Hydrogen Atoms with Ozone from 219-360 K," J. Chem.
Phys. **62**, 350-354 (1976b)
- NASA (1979), Recommendations of the NASA Panel for Data Evaluation,
published in NASA RP 1049 "The Stratosphere: Present and Future,"
E. D. Hudson and E. L. Reed, Editors, Dec. 1979 (report of the
June 1979 Harpers Ferry Workshop),
- Phillips, L. E., and Schiff, H. I., "Mass Spectrometric Studies of
Atomic Reactions. III. Reactions of Hydrogen Atoms with Nitrogen
Dioxide and with Ozone," J. Chem. Phys. **37**, 1233-1238 (1962)
- E. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Uncert Factor
at 298K, notes

| No | Reaction/Reference | Temp. Range/R | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncert Factor at 298K, notes |
|------|---|--------------------|---|---------------------------------|
| 7.19 | $\text{O}_3 + \text{H}_2 + \text{H}_2\text{O} \rightarrow \text{O}_2$ NASA (1979) eval CcdATA (1979) eval | 200-300 220-450 | $\Delta H(298) = -180 \text{ kJ/mol}$ $1.6 \times 10^{-12} \exp(-9400/T)$ $1.9 \times 10^{-12} \exp(-1000/T)$ $\Delta(E/R) = +250, -100$ | 1-25 1-4 |
| | Pavishankara, et al (1979) | 238-357 | $1.8 \times 10^{-12} \exp(-930/T)$ | |
| | Anderson, Kaufman (1973) | 220-450 | $1.3 \times 10^{-12} \exp(-956/T)$ | |
| | Baulch, et al (1976) review | 300 | 6.5×10^{-14} | |
| | DeMore (1975) | 271-333 | $k/k(\text{OH} + \text{CO}) = 16.8 \exp(-1230/T)$ at 700 torr CO_2 | |
| | Kurylo (1973) | 298 | 6.5×10^{-14} | |

The room temperature value is an average of five studies (Anderson and Kaufman (1973); Kurylo (1973); DeMore (1975); Margiten and Anderson (1978); and Ravishankara et al (1979)). The Anderson and Kaufman and Pavishankara et al studies are in excellent agreement on the temperature dependence ($E/R = 955$ and 930 , respectively) and are confirmed by DeMore's data over a more limited range. A recent determination by Zahniser and Howard (1979) is in excellent agreement with our recommendation below room temperature. Their measured rate constants also agree very well with our recommended values at higher temperatures although their data indicates a curved Arrhenius plot over the entire T range.

REFERENCES

- Anderson, J. G., and Kaufman, F., "Kinetics of the Reaction $\text{OH}(v=0) + \text{O}_3 \rightarrow \text{HO}_2 + \text{O}_2$," Chem. Phys. Lett. **12**, 483-486 (1973)
- Baulch, D. L., Drysdale, D. D., Duxbury, J., and Grant, S. J., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 3: Homogeneous Gas Phase Reactions of the $\text{O}_2\text{-O}_3$ System, the $\text{CO-O}_2\text{-H}_2$ System, and of Sulphur-Containing Species," (Butterworths, London, 1976)
- CcdATA(1979). Recommendations of the CcdATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.
- DeMore, W. B., "Rate Constant Ratio for the Reactions of OH with O_3 and CO ," Int. J. Chem. Kinet., Symp. No. 1, 273-279 (1975)
- Kurylo, M. J., "Kinetics of the Reactions $\text{OH}(v=0) + \text{NH}_3 \rightarrow \text{H}_2\text{N} + \text{NH}_2$ and $\text{OH}(v=0) + \text{O}_3 \rightarrow \text{HO}_2 + \text{O}_2$ at 298°K," Chem. Phys. Lett. **23**, 467-471 (1973)

Margitan, Jo J., and Anderson, Jo G., 1978, paper presented at 13th Informal Conference on Photochemistry, Clearwater Beach, Florida, January, 1978

NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA TP 1049 "The Stratosphere: Present and Future."

R. D. Hudson and E. L. Reed, Editors. Deco 1979 (report of the June 1979 Harpers Ferry Workshop).

Pavlishenko, A. R., Wine, P. H., and Langford, A. G., "Absolute Rate Constant for the Reaction $\text{OH}(\nu=0) + \text{O}_3 \rightarrow \text{HO}_2 + \text{O}_2$ over the Temperature Range 238-357°K," J. Chem. Phys. **70**, 984-989 (1979)

Zahniser, M. S., and Howard, C. J., Manuscript to be published, 1979.

P. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY

Uncert Factor
at 298K, notes

| No | Reaction/Reference | Temp- Range/°K | Reaction Rate Constant h/cm ³ molecule ⁻¹ s ⁻¹ | Uncert Factor at 298K, notes |
|------|---|-------------------|--|---------------------------------|
| 7.19 | $\text{O}_3 + \text{H}(\text{v}_1 > 0) \rightarrow \text{products}$ Celiberto, Worley, Potter (1971) | 300 | $\frac{10^{12} \times (300 \text{ K})}{\text{cm}^3}$ | |
| | Streit, Johnston (1976) | | $\frac{\text{cm}^3}{\text{s}}$ | |
| | | | 1.9 ± 0.1 | |
| | | | 2.0 ± 0.9 | |
| | | | 2.8 ± 0.8 | 3.7 ± 0.1 |
| | | | 3.0 ± 0.7 | 4.5 ± 0.1 |
| | | | 5.3 ± 0.6 | 7.0 ± 0.2 |
| | | | 6.5 ± 0.5 | 8.5 ± 0.2 |
| | | | 6.7 ± 0.5 | 8.9 ± 0.2 |
| | | | 7.7 ± 0.3 | 11 ± 0.4 |

The values reported by Streitt and Johnston (1976) are 35% higher than the corresponding values of Coltharp, et al (1971). No selection is made

REFERENCES

- Coltharp, R. W., Worley, S. D., and Potter, A. E., "Reaction Rate of Vibrationally Excited Hydroxyl with Ozon," *Appl. Optics* **10**, 1766-1769 (1971)
- Steit, G. E., and Johnston, R. S., "Reactions and Quenching of Vibrationally Excited Hydroxyl Radicals," *J. Chem. Phys.* **54**, 95-103 (1976)

W. F. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Uncert Factor
at 298K, notes

Reaction Rate Constant
K/cm³molecule⁻¹s⁻¹

Temp.
Range/K

Reaction/Reference

No

| No | Reaction/Reference | Temp. Range/K | Reaction Rate Constant K/cm ³ molecule ⁻¹ s ⁻¹ | Uncert Factor at 298K, notes |
|------|---|------------------|--|---------------------------------|
| | | | | |
| 7.20 | O ₃ + H ₂ O → H ₂ O ₂ | | | |
| | NASA (1979) eval | 200-300 | ΔH (298) = -106 kJ/mol 1.01 x 10 ⁻¹⁴ exp(-580/T) Δ(E/R) = -500, -100 | 1-4 |
| | CODATA (1979) eval | 250-490 | 1.4 x 10 ⁻¹⁴ exp(-(600±200)/T) | 1-5 |
| | Zahniser, Howard (1979) | 250-370 | (1.4±0.4) x 10 ⁻¹⁴ exp(-(580±100)/T) | (a) |
| | DeMore (1979) | 230-334 | k/(k _{ref}) _{0.5} = 6.4 x 10 ⁻⁸ exp(-1220/T) | (a) |
| | Simonaitis, Heicklen (1973b) | 225-298 | k/(k _{ref}) _{0.5} = 1.9 x 10 ⁻⁸ exp(-1000/T) | (a) |
| | DeMore, Tschuikow-Roux (1974) | 273-332 | k/(k _{ref}) _{0.5} = 1.1 x 10 ⁻⁷ exp(-1550±250/T) (a) k _{ref} = k(H ₂ O + H ₂ O ₂ → H ₂ O ₂ + O ₂) | (a) |

The room temperature value is an average of the four reported determinations (Zahniser and Howard (1978); Margitan and Anderson (1978); DeMore and Tschuikow-Roux (1974); and Simonaitis and Heicklen (1973b)). The Zahniser and Howard work is the most direct and, presumably, the best determination and gives E/R = 580. This temperature dependence is confirmed by the last two studies, which were ratios relative to k(H₂O + H₂O₂), when the Cox (1978) E/R value recently reported for that reaction is used, thus lending additional credence to that determination. The A-factor is unusually low. Recent rate constant ratio measurements by DeMore (1979) confirm this recommendation.

REFERENCES

- CODATA(1979). Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.
- Cox, R. A., 1978a, paper presented at WNC Symposium on Ozone, Toronto, June, (1978)
- DeMore, W. B., "Reaction of H₂O with O₃ and the Effect of Water Vapor on H₂O Kinetics," J. Phys. Chem. **83**, 1113-1118 (1979)
- DeMore, W. B., and Tschuikow-Roux, E., "Temperature Dependence of the Reactions of OH and H₂O with O₃," J. Phys. Chem. **78**, 1447-1451 (1974)
- Margitan, J. C., and Anderson, J. G., 1978, paper presented at 13th Informal Conference on Photochemistry, Clearwater Beach, Florida, January, 1978

NASA (1979). Recommendations of the NASA Panel for Data Evaluation,
published in NASA RP 1049 "The Stratosphere: Present and Future,"
R. D. Hudson and E. L. Reed, Editors, Dec. 1979 (report of the
June 1979 Harpers Ferry Workshop).
Simonaitis, R. and Heicklen, J. "The Reaction of NO_2 with O_3 ," J. Phys.,
Chem. 77, 1932-1935 (1973b)
Zahniser, M. S., and Howard, C. J., Manuscript to be published, 1979.
R. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Uncert. Factor
at 250K, notes

Reaction Rate Constant
 $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

Temp.
Range/K

Reaction/Reference

No.

ΔH (298) = -198 kJ/mol

$\text{O}_3 + \text{NO}_2 \rightarrow \text{O}_2 + \text{NO}_3$

$<5 \times 10^{-19}$
 $<5 \times 10^{-19}$
 $<1 \times 10^{-19}$
 $<5 \times 10^{-19}$

258
226
300
300

NASA (1979) eval
Kaiser, Japar (1977)
Streit, et al (1979)

This recommendation is based on the upper limits reported by Kaiser and Japar (1977) and by Streit et al (1979)

REFERENCES

- Kaiser, E. W., and Japar, S. M., "The Kinetics of the Gas Phase Reaction of Nitrous Acid with Ozonene," Chem. Phys. Lett. **22**, 121-124 (1977)
- NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA EP 1049 "The Stratosphere: Present and Future," E. D. Hudson and E. L. Reed, Editors, Dec. 1975 (report of the June 1975 Harpers Ferry Workshop).
- Streit, G. E., Wells, J. S., Fehsenfeld, F. C., and Howard, C. J., "A Tunable Diode Laser Study of the Reactions of Nitric and Nitrous Acids: $\text{NO}_3 + \text{NO}$ and $\text{NO}_3 + \text{NO}_2$," J. Chem. Phys. **78**, 3435-3443 (1979)

E. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY
 PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No | Reaction/Reference | Temp. Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncert Factor at 298K, notes |
|------|--|--------------------|---|---------------------------------|
| 7.27 | O ₃ + SO → SO ₂ + SO ₂ CODATA (1979) eval Schofield (1973) review Baulch et al (1976) review | 220-300 223-303 | ΔH (298) = -445 kJ/mol 2.5 x 10 ⁻¹² exp(-(1100±400)/T) 2.5 x 10 ⁻¹² exp(-1050/T) no recommendation | 2 |

There is only one reported value for this rate constant. See the reviews by Schofield (1973) and Baulch, et al (1976)

REFERENCES

- Baulch, D. L., Drysdale, D. R., Duxbury, J., and Grant, S. J., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 3: Homogeneous Gas Phase Reactions of the O₂-O₃ System, the CO-O₂-H₂ System, and of Sulphur-Containing Species," (Butterworths, London, 1976)
- CODATA(1979): Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.
- Schofield, K., "Evaluated Chemical Kinetic Rate Constants for Various Gas Phase Reactions," J. Phys. Chem. Ref. Data **2**, 25-84 (1973)

R. F. Hampson
 June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No | Reaction/Reference | Temp. Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncert. Factor at 298K, notes |
|------|--|------------------|--|----------------------------------|
| 7,28 | O ₃ + SO ₂ → SO ₃ + O ₂ Davis, Prusaczyk, Dwyer, Kim (1974) Daubendiek, Calvert (1974) | 300 300 | ΔH (298) = -242 kJ/mol k < 2 x 10 ⁻²² k < 8 x 10 ⁻²⁴ | preliminary |

Note that this is an upper limit only

REFERENCES

- Daubendiek, P. L., and Calvert, J. G., "A Study of the N₂O₅-SO₂-O₃ Reaction System," Environ. Lett. **2**, 103-116 (1975)
- Davis, Dr. D., Prusaczyk, J., Dwyer, M., and Kim, P., "A Stop-Flow Time of Flight Mass Spectrometry Kinetics Study: Reaction of Ozone with Nitrogen Dioxide and Sulfur Dioxide," J. Phys. Chem. **78**, 1775-1779 (1974)

R. F. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No | Reaction/Reference | Temp. Range/K | Reaction Rate Constant $k/\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ | Uncert Factor at 298K, notes |
|------|--|------------------|--|---------------------------------|
| 7.32 | $\text{O}_3 + \text{H}_2\text{S} \rightarrow \text{products}$ Glavas, Toby (1975) Becker, Inocencio, Schurath (1975) | 298-343 300 | $7 \times 10^{-14} \exp(-3400/T)$ $< 2 \times 10^{-20}$ | |

No recommendation is made because of the disagreement between these results - the room temperature value of Glavas and Toby (1975) is a factor of 40 higher than the upper limit reported by Becker, et al (1975)

REFERENCES

- Becker, E. E., Inocencio, M., and Schurath, U., "The Reaction of Ozone with Hydrogen Sulfide and its Organic Derivatives," *Int. J. Chem. Kinet. Symp.* No. 1, 205-220 (1975)
- Glavas, S., and Toby, S., "The Reaction between Ozone and Hydrogen Sulfide: Kinetics and Effect of Added Gases," *Am. Chem. Soc., ACS Symp. Series* 17, 122-131 (1975)

E. F. Hampson
May 1976

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No | Reaction/Reference | Temp- Range/K | Reaction Rate Constant $k/cm^3 \text{ molecule}^{-1} s^{-1}$ | Uncert. Factor at 298K, notes |
|------|------------------------|------------------|---|----------------------------------|
| 7.35 | $O_3 + Cl + ClO + O_2$ | | $\Delta H (298) = -162 \text{ kJ/mol}$ | |
| | NASA (1979) eval | 200-300 | $2.8 \times 10^{-11} \exp(-(257 \pm 100)/T)$ | 1.15 |
| | CODATA (1979) | 205-298 | $2.7 \times 10^{-11} \exp(-(257 \pm 100)/T)$ | 1.15 |
| | Watson (1977) review | 205-298 | $2.7 \times 10^{-11} \exp(-257/T)$ | |
| | Clyne, Nip (1976a) | 221-629 | $5.18 \times 10^{-11} \exp(-418/T)$ | |
| | Kurylo, Braun (1976) | 213-298 | $2.72 \times 10^{-11} \exp(-298/T)$ | |
| | Watson, et al (1976) | 220-350 | $3.08 \times 10^{-11} \exp(-290/T)$ | |
| | Zahniser, et al (1976) | 210-360 | $2.17 \times 10^{-11} \exp(-171/T)$ | |

Discharged from NASA 1010. The results reported for $k(298 \text{ K})$ by Watson et al (1976), Zahniser et al (1976), Kurylo and Braun (1976a) and Clyne and Nip (1976a) are in good agreement, and have been used to determine the preferred value at this temperature. The values reported by Leu and DeMore (1976) (due to the wide error limits) and Clyne and Watson (1974a) (the value is inexplicably high) are not considered. The four Arrhenius expressions are in fair agreement within the temperature range 205-300 K. In this temperature range, the rate constants at any particular temperature agree to within (30-40)%. Although the values of the activation energy obtained by Watson et al, and Kurylo and Braun are in excellent agreement, the value of k in the study of Kurylo and Braun is consistently ($\approx 17\%$) lower than that of Watson et al. This may suggest a systematic underestimate of the rate constant, as the value of the other three studies agree so well at 298 K. A more disturbing difference is the scatter in the values reported for the activation energy (338-631 cal mole $^{-1}$). However, there is no reason to prefer any one set of data to any other; therefore, the preferred Arrhenius expression shown above was obtained by computing the mean of the four results between 205 and 298 K. Inclusion of higher temperature ($\pm 466 \text{ K}$) experimental data would yield the following Arrhenius expression: $k = (3.34 \pm 1.0) \times 10^{-11} \exp(-(310 \pm 76)/T)$

REFERENCES

- Clyne, W. A., A., and Nip, W. S., "Study of Elementary Reactions by Atomic Resonance Absorption with a Non-Reversed Source Part 1 - The Reaction $Cl + O_3 \rightarrow ClO + O_2$," *J. Chem. Soc., Faraday Trans. II* **72**, 838-847 (1976a)
- Clyne, W. A., A., and Watson, R. T., "Kinetic Studies of Diatomic Free Radicals using Mass Spectrometry Part 2, Rapid Bimolecular Reactions Involving the $ClO X^2\Pi$ Radical," *J. Chem. Soc., Faraday Trans. II* **70**, 2250-2259 (1974a)
- CODATA(1979). Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.

- Kurylo, M. J., and Braun, W., "Flash Photolysis Resonance Fluorescence Study of the Reaction $\text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2$ over the Temperature Range 213-298 K," *Chem. Phys. Lett.* **37**, 232-235 (1976)
- Leu, M.-F., and DeMore, W. E., "Rate Constants at 295 K for the Reactions of Atomic Chlorine with H_2O_2 , HO_2 , O_3 , CH_4 and HNO_2 ," *Chem. Phys. Lett.* **41**, 121-124 (1976)
- NASA RP-1010, "Chlorofluoromethanes and the Stratosphere" R. D. Hudson, Editor, August 1977 This reference contains the NASA (1977) rate constant recommendations.
- NASA (1979), Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," R. D. Hudson and E. L. Reed, Editors, Deco 1979 (report of the June 1979 Harpers Ferry Workshop).
- Watson, R., Machado, G., Fischer, E., and Davis, D. D., "A Temperature Dependence Kinetics Study of the Reaction of $\text{Cl}(\text{P}_{3/2})$ with O_3 , CH_4 and H_2O_2 ," *J. Chem. Phys.* **65**, 2126-2138 (1976)
- Watson, R. T., "Rate Constants for Reactions of ClO_2 of Atmospheric Interest," *J. Phys. Chem. Ref. Data* **6**, 871-918 (1977)
- Zahniser, M. E., Kaufman, F., and Anderson, J. G., "Kinetics of the Reaction $\text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2$," *Chem. Phys. Lett.* **31**, 226-231 (1976)

R. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No | Reaction/Reference | Temp. Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncert. Factor at 298K, notes |
|--------|--|------------------|--|----------------------------------|
| 7.35Br | O ₃ + Br → BrO + O ₂ | | ΔH (298) = -129 kJ/mol | |
| | NASA (1979) eval | 200-300 | 1.4 x 10 ⁻¹¹ exp(-(755±200)/T) | 1-2 |
| | CODATA (1979) eval | 220-360 | 1.4 x 10 ⁻¹¹ exp(-(760±200)/T) | 1-25 |
| | Leu, DeMore (1977) | 224-422 | 3.34 x 10 ⁻¹¹ exp(-578/T) | |
| | Michael, et al (1978) | 200-360 | 7.74 x 10 ⁻¹² exp(-603/T) | |
| | Michael, Payne (1979) | 234-360 | 9.45 x 10 ⁻¹² exp(-659/T) | |
| | Clyne, Watson (1975) | 298 | 1.2 x 10 ⁻¹² | |

Changed from NASA 1010 due to new data. The results reported for k(298 K) by Clyne and Watson (1975), Leu and DeMore (1977), Michael et al (1978) and Michael and Payne (1978) are in excellent agreement. The preferred value at 298 K is derived by taking a simple mean of these four values. The temperature dependences reported for k by Leu and DeMore, Michael et al and Michael and Payne can only be considered to be in fair agreement. There is a spread of 25% in k at 220 K and 50% at 360 K. Although the results reported by Michael et al and Michael and Payne are in good agreement, there is no reason at present to discard the results of Leu and DeMore. Therefore, until further results are reported, the preferred value should be synthesized to best fit all the data reported from these four studies.

REFERENCES

Clyne, W. A., and Watson, R. T., "Kinetics Studies for Diatomic Free Radicals using Mass Spectrometry Part 3 - Elementary Reactions Involving BrO X²Π Radicals," J. Chem. Soc., Faraday Trans. I 71, 336-350 (1975)

CODATA(1979). Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data

Leu, W.-T., and DeMore, W. B., "Rate Constant for the Reaction of Atomic Bromine with Ozone," Chem. Phys. Lett. 42, 317-320 (1977)

Michael, J. V., Lee, J. H., Payne, W. A., and Stief, L. J.,

"Absolute Rate of the Reaction of Bromine Atoms with Ozone from 200-360 K," J. Chem. Phys. 68, 4093-4097 (1978)

Michael, J. V., and Payne, W. A., "Absolute Rate Constants for the Reaction of Bromine Atoms with Ozone from 234 to 360K," Int. J. Chem. Kinet. 11, 799-809 (1979)

W. P. Rasmussen
June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Temp. Range/K | Reaction Rate Constant M/cm ³ molecule ⁻¹ s ⁻¹ | Uncert. Factor at 298K, notes |
|-------|---|------------------|--|----------------------------------|
| 7.35F | $\text{O}_3 + \text{F} \rightarrow \text{F}\text{O} + \text{O}_2$ | | | |
| | NASA (1979) eval | 200-300 | $2.0 \times 10^{-11} \exp(-22600/T)$ | 2 |
| | CODATA (1979) eval | 250-365 | $2.0 \times 10^{-11} \exp(-22600/T)$ | 2 |
| | Wagner, et al (1972) | 253-365 | $2.0 \times 10^{-11} \exp(-22600/T)$ | |

New entry. The only experimental data is that reported by Wagner et al (1972). Value appears to be quite reasonable in view of the well known reactivity of atomic chlorine with O_3

REFERENCES

CODATA(1979). Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.

NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," R. D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the June 1975 Harpers Ferry Workshop).

Wagner, H. Gg., Zetzsch, C., and Wornatz, J. "Gas-Phase Preparation of OF Radicals by Reaction of Fluorine Atoms with Ozone," Ber. Bunsenges. Phys. Chem. **76**, 526-530 (1972)

R. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY

REPORTS BY CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Uncert Factor
at 298K, notes

Reaction Rate Constant
k/cm³molecule⁻¹s⁻¹

Temp
Range/K

Reaction/Reference

| | |
|----------------------|---|
| 10 - 200 °C (a) | ΔH (298) = -148 kJ/mol |
| 100 - 200 °C (b) | = -156 kJ/mol |
| 200-300 | k _a < 1 x 10 ⁻¹² exp(-4000/T) |
| 200-300 | k _b < 1 x 10 ⁻¹² exp(-4000/T) |
| 300 | < 5 x 10 ⁻¹⁵ |
| DeMore (1977) review | |

Unchanged from NASA 1010. The branching ratio between the two channels is not well-defined, but, for the present discussion, is assumed to be unity. The Arrhenius expressions were estimated on the basis of data reported by DeMore, Lin and Jaffe (1976)

REFERENCES

- DeMore, W. B., Lin, C. L., and Jaffe, S., Results presented at 12th Informal Conference on Photochemistry, Washington, D.C., (1976)
- NASA RP-1010, "Chlorofluoromethanes and the Stratosphere" E. D. Hudson, Editor, August 1977 This reference contains the NASA (1977) rate constant recommendations.
- NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future."
- E. D. Hudson and E. L. Reed, Editors, Deco 1979 (report of the June 1979 Harpers Ferry Workshop).
- Watson, R. L., "Rate Constants for Reactions of ClO₂ of Atmospheric Interest," J. Phys. Chem. Ref. Data 6, 871-918 (1977)
- V. P. Karpman
June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No | Reaction/Reference | Temp. Range/K | Reaction Rate Constant $k/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$ | Uncert. Factor at 298K, notes |
|--------|--|------------------|--|----------------------------------|
| 7.36Br | $\text{O}_3 + \text{Br} \cdot \rightarrow \text{Br} + 2\text{O}_2$ | | | |
| | NASA (1979) eval | 200-300 | $k < 1 \times 10^{-12}$ | 3 |
| | CODATA (1979) eval | 298 | $k < 5 \times 10^{-15}$ | 3 |
| | Sander, Watson (1978) | 298 | $k < 5 \times 10^{-15}$ | |
| | Clyne, Cruse (1970) | 293 | $k < 8 \times 10^{-14}$ | |

$\Delta H(298) = -157 \text{ kJ/mol}$

Changed from NASA 1010. Based on a study reported by Sander and Watson (1978). Clyne and Cruse (1970a) also reported an upper limit of $8 \times 10^{-14} \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1}$ for this reaction. Both studies reported that there is no evidence for this reaction. The analogous ClO reaction has a rate constant of $\sim 10^{-18} \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1}$

REFERENCES

Clyne, M. A. A., and Cruse, M. W., "Rates of Elementary Reaction Involving the $\text{BrO}(\text{X}^2\Pi)$ and $\text{IO}(\text{X}^2\Pi)$ Radicals. Part 1: Formation and Decay of the BrO Radical," *Trans. Faraday Soc.* **66**, 2214-2226 (1970a)

CODATA(1979). Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.

NASA RP-1010. "Chlorofluoromethanes and the Stratosphere"
R. D. Hudson, Editor, August 1977 This reference contains the NASA (1977) rate constant recommendations.
NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future."
R. D. Hudson and E. L. Reed, Editors, Dec. 1979 (report of the June 1979 Harpers Ferry Workshop).

Sander, S. P., and Watson, R. To. 1978., Manuscript in preparation

R. P. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Uncert. Factor
at 298K, notes

Reaction/Reference

Temp.
Range/K

Reaction Rate Constant
k/cm³molecule⁻¹s⁻¹

No.

7.36F
O₃ + F₂ → F + 2O₂ (a)
→ F₂ + O₂ (b)
NASA (1979) eval
CODATA (1976) eval
Δ (298) = -172 kJ/mol
= -239 kJ/mol
no recommendation; see note
No recommendation

New entry. The F₂ + O₃ reaction has two possible pathways which are exothermic, resulting in the production of F + 2O₂ or F₂ + O₂. Although this reaction has not been studied in a simple direct manner, two studies of complex chemical systems have inferred some kinetic information about it. Starrieco et al (1962) measured quantum yields for ozone destruction in F₂/O₃ mixtures, and attributed the high values, ~4600, to be due to the rapid regeneration of atomic fluorine via the F₂ + O₃ → F + 2O₂ reaction. However, their results are probably also consistent with the chain propagation process being F₂ + F₂ → 2F + O₂ (the latter reaction has been studied twice (Wagner et al (1972), Clyne and Watson (1974b)), but although the value of [F]_{produced}/[F₂]_{consumed} is known to be close to unity, it has not been accurately determined. Consequently it is impossible to ascertain from the experimental results of Starrieco et al whether or not the high quantum yields for ozone destruction should be attributed to the F₂ + O₃ reaction producing either F + 2O₂ or F₂ + O₂ (this process is also a chain propagation step if the resulting F₂ radical preferentially reacts with ozone rather than with either F₂ or itself). Wagner et al utilized a low pressure discharge flow-mass spectrometric system to study the F + O₃ and F₂ + F₂ reactions by directly monitoring the time history of the concentrations of F, F₂ and O₃. They concluded that the F₂ + O₃ reaction was unimportant in their system. However, their paper does not present enough information to warrant this conclusion. Indeed, their value of k(F₂ + F₂) of 3 × 10⁻¹¹ is about a factor of 4 greater than that reported by Clyne and Watson, which may possibly be attributed to either reactive impurities being present in their system, e.g., O₃ or that the F₂ + O₃ reactions were not of negligible importance in their study. Consequently, it is not possible to determine a value for the F₂ + O₃ reaction rate constant from existing experimental data. It is worth noting that the analogous Cl₂ + O₃ reactions are extremely slow (~10⁻¹⁶ cm³molecule⁻¹s⁻¹) DeMore et al (1976), and an upper limit of 8 × 10⁻¹⁴ Clyne and Cruse (1970a) and 5 × 10⁻¹⁵ cm³molecule⁻¹s⁻¹ Sander and Watson (1978) have been reported for Br₂ + O₃.

REFERENCES

- Clyne, M. A. A., and Cruse, H. W., "Rates of Elementary Reaction Involving the Br₂(¹Δ_{g) and I₂(¹Δ_{g) Radicals. Part 1: Formation and Decay of the Br₂ Radical," *Trans. Faraday Soc.* **66**, 2214-2226 (1970a)}}
- Clyne, M. A. A., and Watson, E. I., "Kinetic Studies of Diatomic Free Radicals using Mass Spectrometry Part 1. System Description and Applications to F Atoms and F₂ Radicals," *J. Chem. Soc., Faraday Trans. I* **70**, 1109-1123 (1974)
- CDATA(1975), Recommendations of the CDATA Task Group on Chemical Kinetics. To be published in the *Journal of Physical and Chemical Reference Data*.
- DeMore, W. B., Lin, C. I., and Jaffe, S., Results presented at 12th Informal Conference on Photochemistry, Washington, D.C. (1976)
- NASA (1979), Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," E. D. Hudson and E. I. Reed, Editors, Dec. 1975 (report of the June 1975 Harpers Ferry Workshop).
- Sander, S. P., and Watson, E. I., 1979, Manuscript in preparation.
- Staricco, E. B., Sirci, J. E., and Schuster, B. J., "Die Photochemische Reaktion Zwischen Fluor und Ozon," *Z. Phys. Chemie N.F.* **21**, 385-396 (1962)
- E. E. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No | Reaction/Reference | Temp. Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncert Factor at 298K, notes |
|------|--|------------------|--|---------------------------------|
| 7.45 | C ₃ + C ₆ → C ₆ D ₂ + C ₂ Arim, Warnock (1972) | 296 | ΔH (298) = -426 kJ/mol 4 × 10 ⁻²⁵ | |

Note that this is an upper limit only

REFERENCES

Arim, L. M., and Warnock, P., "Reaction of Ozone with Carbon Monoxide,"
J. Phys. Chem. **76**, 1514-1515 (1972)
R. P. Hampson
May 1978

A-4 CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No | Reaction/Reference | Temp. Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncert Factor at 298K, notes |
|------|--|------------------|--|---------------------------------|
| 7.08 | C ₃ + CH ₂ O → products Breslavsky, Reichlen (1976) | 300 | 42 x 10 ⁻²⁴ | |

Note that this is an upper limit only for the gas phase reaction

REFERENCES

Breslavsky, S., and Reichlen, J., "The Gas-Phase Reaction of C₃ with H₂CO,"
Int. J. Chem. Kinet. 8, 801-808 (1976)

S. P. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No | Reaction/Reference | Temp Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncert Factor at 298K, notes |
|------|---|-----------------|---|---------------------------------|
| 7.49 | $\text{C}_3 + \text{CH}_3 \rightarrow \text{CH}_3\text{C} + \text{C}_2$ (a) $\rightarrow \text{CH}_2\text{C} + \text{HC}_2$ (b) Simonaitis, Heicklen (1975) | 221-298 | ΔH (298) = -274 kJ/mol ΔH = -395 kJ/mol $(k_a + k_b)/k_{\text{ref}} = 12 \exp(-525/T)$ (a) k_{ref} is 2nd order high pressure limit for $\text{CH}_3 + \text{O}_2(+M) \rightarrow \text{CH}_3\text{O}_2(+M)$ | (a) |

Only reported value - no recommendation. Authors suggest that channel (a) is major, if not exclusive, reaction pathway

REFERENCES

- Simonaitis, R., and Heicklen, J., "Reactions of CH_3 , CH_3O , and CH_3O_2 Radicals with C_3 ," J. Phys. Chem. **79**, 298-302 (1975)
- R. F. Hampson
 May 1978

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No | Reaction/Reference | Temp. Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncert. Factor at 298K, notes |
|------|--|------------------|--|----------------------------------|
| 7.51 | $\text{O}_3 + \text{CH}_3\text{O}_2 \rightarrow \text{products}$ Simionaitis, Heicklen (1975) | 300 | 42.4×10^{-17} | |

Note that this is an upper limit only

REFERENCES

Simionaitis, R., and Heicklen, J., "Reactions of CH_3 , CH_3O , and CH_3O_2 Radicals with O_3 ," J. Phys. Chem. **79**, 298-302 (1975)

R. P. Hampson
May 1976

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No | Reaction/Reference | Temp. Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncert. Factor at 298K, notes |
|------|---|------------------|--|----------------------------------|
| 7.54 | $O_3 + CH_3ONO \rightarrow CH_3ONO_2 + O_2$ Hastie, et al (1976) | 298-325 | $\Delta H (298) = -197 \text{ kJ/mol}$ $6.2 \times 10^{-13} \exp(-5315/T)$ | |

Only reported value - no recommendation

REFERENCES

Hastie, D. R., Freeman, C. G., McEwan, W. J., and Schiff, H. I., "The
Reactions of Ozone with Methyl and Ethyl Nitrites," Int. J. Chem. Kinet.
8, 307-313 (1976)

V. P. Wampson
May 1978

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No | Reaction/Reference | Temp. Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncert Factor at 298K, notes |
|------|--|------------------|--|---------------------------------|
| 7.56 | O ₃ + CH ₄ → products Dillamuth, et al (1960) | 310-340 | 2.7 × 10 ⁻¹³ exp (-7700/T) | |

only reported value - no recommendation

REFERENCES

Dillamuth, F. J., Skidmore, D., Ro., and Schubert, C. C., "The Reaction of
Ozone with Methane," J. Phys. Chem. **64**, 1496-1495 (1960)

R. P. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Uncert. Factor
at 298K, notes

| No | Reaction/Reference | Temp. Range/K | Reaction Rate Constant $k/\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ | Uncert. Factor at 298K, notes |
|------|---|------------------|--|----------------------------------|
| 7.57 | $\text{O}_3 + \text{C}_2\text{H}_4 \rightarrow \text{products}$ | | | |
| | Herron, Hule (1974) | 235-362 | $9.0 \times 10^{-15} \exp(-2560/T)$ | 1-3 |
| | Demerjian, et al (1974) review | 300 | 2.7×10^{-18} | |
| | Demore (1969) | 178-233 | $3.2 \times 10^{-15} \exp(-2400/T)$ | |
| | Stedman, et al (1973) | 300 | $1.55 \pm 0.15 \times 10^{-18}$ | |
| | Becker, Schurath, Seltz (1974) | 280-360 | $1.2 \times 10^{-14} \exp(-2490 + 100/T)$ | |
| | Japar, Wu, Miki (1974) | 298 | $1.5 \pm 0.1 \times 10^{-18}$ | |
| | Toby, et al (1976) | 303 | $1.7 \pm 0.1 \times 10^{-18}$ | |

This evaluation accepts the results of Herron and Hule (1974), which were determined in the presence of excess O_2 . Dioxirane has been identified as a product at low temperature; see Lovas and Suenram (1977) and Martinez et al (1977)

REFERENCES

- Becker, K. E., Schurath, U., and Seltz, R., "Ozone-Gleixin Reactions in the Gas Phase: I. Rate Constants and Activation Energies," *Int. J. Chem. Kinet.* **5**, 725-739 (1974)
- Demerjian, K. L., Kerr, J. A., and Calvert, J. G., "The Mechanism of Photochemical Smog Formation," *Adv. Environ. Sci. Technol.* **5**, 1-262 (1974)
- J. M. Pitts, Jr., and R. L. Metcalfe, editors, Wiley-Interscience
- Demore, V. R., "Arrhenius Constants for the Reactions of Ozone with Ethylene and Acetylene," *Int. J. Chem. Kinet.* **1**, 209-220 (1969)
- Herron, J. T., and Hule, R. R., "Rate Constants for the Reactions of Ozone with Ethene and Propene, from 235.0 to 362.0 K," *J. Phys. Chem.* **78**, 2085-2088 (1974)
- Japar, S. M., Wu, C. H., and Miki, R., "Rate Constants for the Reaction of ozone with olefins in the Gas Phase," *J. Phys. Chem.* **78**, 2318 (1974)

- Iovae, P. J., and Suarez, R. D., "Identification of Dioxirane (H_2CO_3)
 in Ozone-Glefin Reactions Via Microwave Spectroscopy," *Chem. Phys. Lett.* **51**, 453-456 (1977)
- Martinez, P. I., Huie, R. E., and Herron, J. T., "Mass Spectrometric
 Detection of Dioxirane, H_2CO_3 , and its Decomposition Products, H_2
 and CO , from the Reaction of Ozone with Ethylene," *Chem. Phys. Lett.*
51, 457-459 (1977)
- Stedman, D. R., Wu, C. H., and Niki, S., "Kinetics of Gas-Phase Reactions
 of Ozone with Some Olefins," *J. Phys. Chem.* **77**, 2511-2514 (1973)
- Toby, R. S., Toby, B., and G'Neal, R. E., "The Kinetics of the Gas-Phase
 Reaction between Ozone and Alkenes," *Int. J. Chem. Kinet.* **8**, 25-35 (1976)
- W. F. Hampson
 May 1978

CHEMICAL KINETICS DATA SURVEY
 PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Uncert. Factor
at 298K, notes

7.59 $O_3 + C_3H_6 \rightarrow$ products

| Reaction/Reference | Temp. Range/K | Reaction Rate Constant $k/cm^3 \text{ molecule}^{-1} s^{-1}$ | Uncert. Factor at 298K, notes |
|--------------------------------|---------------|---|----------------------------------|
| Herron, Hule (1974) | 235-362 | $6.1 \times 10^{-15} \exp(-1900/T)$ | 1.3 |
| Demerjian et al (1974) review | 300 | 1.0×10^{-17} | (a) |
| DeMore (1969) | 183, 153, 300 | $1.6 \times 10^{-15} \exp(-1600/T)$ | |
| Stedman, et al (1973) | 300 | 1.25×10^{-17} | |
| Recker, Schurath, Seltz (1974) | 280-360 | $1.1 \times 10^{-14} \exp(-1970 + 100/T)$ | |
| Japar, Wu, Niki (1974) | 298 | 1.30×10^{-17} | |
| | | (a) Includes 300 K point of Hanst et al (1958) | |

This evaluation accepts the results of Herron and Hule (1974), which were determined in the presence of excess O_2

REFERENCES

- Becker, K. E., Schurath, U., and Seltz, H., "Ozone-declin Reactions in the Gas Phase: 1. Rate Constants and Activation Energies," *Int. J. Chem. Kinet.* **6**, 725-739 (1974)
- Demerjian, K. L., Kerr, J. A., and Calvert, J. G., "The Mechanism of Photochemical Smog Formation," *Adv. Environ. Sci. Technol.* **4**, 1-262 (1974)
- J. N. Pitts, Jr., and R. L. Metcalf, editors, *Wiley-Interscience*
- DeMore, W. B., "Arrhenius Constants for the Reactions of Ozone with Ethylene and Acetylene," *Int. J. Chem. Kinet.* **1**, 209-220 (1969)
- Hanst, P. L., Stephens, E. R., Scott, W. E., and Doerr, F. C., "Atmospheric Ozone-declin Reactions," (The Franklin Institute, Philadelphia, Pa. 1958)
- Herron, J. T., and Hule, R. E., "Rate Constants for the Reactions of Ozone with Ethene and Propene, from 235.0 to 362.0 K," *J. Phys. Chem.* **78**, 2085-2088 (1974)
- Japar, S. M., Wu, C. H., and Niki, H., "Rate Constants for the Reaction of Ozone with Olefins in the Gas Phase," *J. Phys. Chem.* **78**, 2318 (1974)
- Stedman, D. H., Wu, C. H., and Niki, H., "Kinetics of Gas-Phase Reactions of Ozone with Some Olefins," *J. Phys. Chem.* **77**, 2511-2514 (1973)
- W. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No | Reaction/Reference | Temp Range/K | Reaction Rate Constant $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | Uncert Factor at 298K, notes |
|------|---|-----------------|--|---------------------------------|
| 7.59 | C_3 + allene - products Toby, Toby (1974) | 226-325 | $1.6 \times 10^{-15} \exp(-2750/T)$ (a) Mechanism discussed in Toby and Toby (1975) and Toby, et al (1976) | (a) |

Only one reported value - no recommendation

REFERENCES

- Toby, F. S., and Toby, S., "Reaction between Ozone and Allene in the Gas Phase,"
Int. J. Chem. Kinet. **8**, 417-428 (1974)
- Toby, F. S., and Toby, S., "The Reaction of Ozone with 1,3-Butadiene and with
Allene," Int. J. Chem. Kinet., Symp. No 1, 197-204 (1975)
- Toby, F. S., Toby, S., and O'Neal, K. E., "The Kinetics of the Gas-Phase
Reaction between Ozone and Alkenes," Int. J. Chem. Kinet. **8**, 25-35 (1976)

R. F. Hampson
June 1979

AD-A091 631

NATIONAL BUREAU OF STANDARDS WASHINGTON DC CHEMICAL --ETC F/G 4/1
CHEMICAL KINETIC AND PHOTOCHEMICAL DATA SHEETS FOR ATMOSPHERIC --ETC
APR 80 R F HAMPSON

DOT-FA79WA1-005

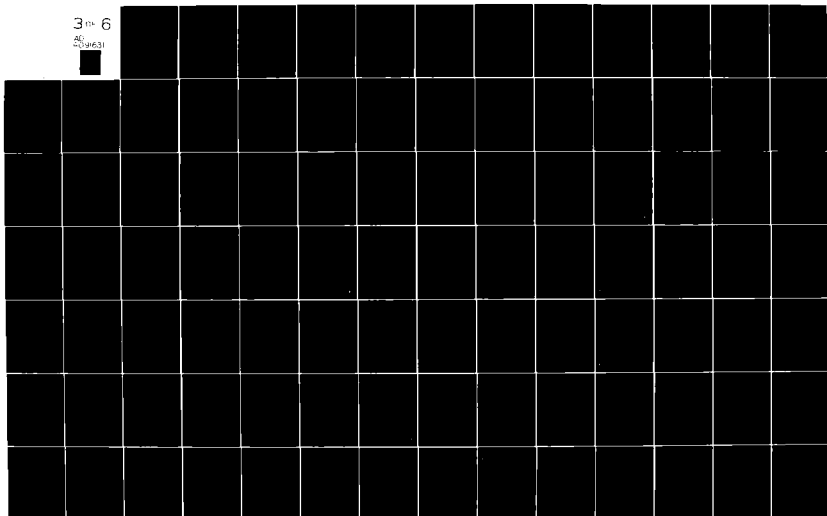
UNCLASSIFIED

FAA/EE-80-17

NL

3 of 6

AD-A091 631



CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No | Reaction/Reference | Temp. Range/K | Reaction Rate Constant $k/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$ | Uncert Factor at 298K, notes |
|------|---|------------------|--|---------------------------------|
| 7.59 | C_3 + 1-butene \rightarrow products Hule, Herron (1975) Japar, Wu, Niki (1974) | 225-363 298 | $2.9 \times 10^{-15} \exp(-1690/T)$ 1.23×10^{-17} | 1-3 |

This evaluation accepts the results of the temperature dependent study of Hule and Herron (1975) with error limits to encompass the 20% higher room temperature result of Japar, et al (1974)

REFERENCES

- Hule, P. E., and Herron, J. To. "Temperature Dependence of the Rate Constants for Reactions of Ozone with Some Olefins," Int. J. Chem. Kinet., Symp. No. 1, 165-181 (1975)
- Japar, S., Mc. Wu, Co. Ho., and Niki, H., "Rate Constants for the Reaction of Ozone with Olefins in the Gas Phase," J. Phys. Chem. 78, 2318 (1974)
- G. F. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No | Reaction/Reference | Temp Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncert Factor at 298K, notes |
|------|---|-----------------|--|---------------------------------|
| 7.59 | O ₃ + cis-2-butene → products Hule, Herron (1975) Japar, Wu, Niki (1974) | 225-363 298 | 3.1 x 10 ⁻¹⁵ exp(-960/T) 1.61 x 10 ⁻¹⁶ | 1-3 |

This evaluation accepts the results of the temperature dependent study of Hule and Herron (1975) with error limits to encompass the 50% higher room temperature result of Japar, et al (1974)

REFERENCES

- Hule, R. E., and Herron, J. T., "Temperature Dependence of the Rate Constants for Reactions of Ozone with Some Olefins," Int. J. Chem. Kinet., Symp. No. 1, 165-181 (1975)
- Japar, S. M., Wu, C. H., and Niki, K., "Rate Constants for the Reaction of Ozone with Olefins in the Gas Phase," J. Phys. Chem. 78, 2318 (1974)

R. F. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Uncert Factor
at 298K, notes

Reaction/Reference

Temp.
Range/K

Reaction Rate Constant
 $k/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$

No

7.59

$\text{O}_3 + \text{trans-2-butene} \rightarrow \text{products}$

*Rule, Herron (1975)

Japar, Wu, Niki (1974)

225-363

298

$6.0 \times 10^{-15} \exp(-1050/T)$
 2.60×10^{-16}

1-5

This evaluation accepts the results of the temperature dependent study of Rule and Herron (1975) with error limits to encompass the 50% higher room temperature result of Japar, et al (1974)

REFERENCES

Rule, P. E., and Herron, J. To, "Temperature Dependence of the Rate Constants for Reactions of Ozone with Some Olefins," Int. J. Chem. Kinet.

Symp. No. 1, 165-181 (1975)

Japar, S. M., Wu, C. H., and Niki, H., "Rate Constants for the Reaction of Ozone with Olefins in the Gas Phase," J. Phys. Chem. **78**, 2318 (1974)

R. F. Hampson

May 1976

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No | Reaction/Reference | Temp. Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncert. Factor at 298K, notes |
|------|---|--------------------------------------|---|----------------------------------|
| 7.59 | O ₃ + 1,3-butadiene → products This survey Toby, Toby (1975) Becker, Schurath, Seitz (1974) Japar, Wu, Niki (1974) | 270-360 273-343 280-360 298 | 6 x 10 ⁻¹⁴ exp(-2900/T) 1 x 10 ⁻¹³ exp(-2900/T) 5.4 x 10 ⁻¹⁴ exp(-2660/T) 8.4 x 10 ⁻¹⁶ | 1-3 ±0-5 |

The recommended expression was derived by averaging the three room temperature values and averaging the two temperature dependences. The preexponential factor was then derived to fit the room temperature value

REFERENCES

- Becker, K. E., Schurath, U., and Seitz, E., "Ozone-Glefin Reactions in the Gas Phase. I. Rate Constants and Activation Energies," Int. J. Chem. Kinet. **5**, 725-739 (1974)
- Japar, S. M., Wu, C. E., and Niki, E., "Rate Constants for the Reaction of Ozone with Olefins in the Gas Phase," J. Phys. Chem. **78**, 2318-2320 (1974)
- Toby, F. S., and Toby, S., "The Reaction of Ozone with 1,3-Butadiene and with Allene," Int. J. Chem. Kinet., Symp. No 1, 197-204 (1975)
- B. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No | Reaction/Reference | Temp. Range/° | Reaction Rate Constant $k/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$ | Uncert. Factor at 298K, notes |
|------|--|------------------|--|----------------------------------|
| 7.64 | $\text{O}_3 + \text{cis-C}_2\text{Cl}_2\text{H}_2 \rightarrow \text{products}$ Blume et al (1976) | 296 | 3.7×10^{-20} | |

Only reported value - no recommendation

REFERENCES

Blume, C. W., Hiestune, I. C., and Heicklen, J., "Gas-Phase Ozonolysis of
Cis- and Trans-Dichloroethylene," *Int. J. Chem. Kinet.* **8**, 235-258 (1976)
R. F. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No | Reaction/Reference | Temp. Range/K | Reaction Rate Constant $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | Uncert. Factor at 298K, notes |
|------|--|------------------|--|----------------------------------|
| 7.64 | $\text{C}_3 + \text{trans-C}_2\text{Cl}_2\text{H}_2 \rightarrow \text{products}$ Blume et al (1976) | 296 | 2.5×10^{-19} | |

Only reported value - no recommendation

REFERENCES

Blume, C. W., Hiestand, I. C., and Heicklen, J. G. "Gas-Phase Ozonolysis of
Cis- and Trans-Dichloroethylene," Int. J. Chem. Kinet. 8, 235-258 (1976)

R. F. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No | Reaction/Reference | Temp. Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncert. Factor at 298K, notes |
|--------------|---|------------------|--|----------------------------------|
| 8, 9, 12, 13 | N + N ₂ → N ₂ + N (r) N ₂ + N → N ₂ + N (r) Baulch, et al (1973) review | 100-600 | ΔH (298) = -945 kJ/mol k _f = 8.3 x 10 ⁻³⁴ exp(+500/T) cm ⁶ molecule ⁻² s ⁻¹ M = N ₂ k _f = 6.4 x 10 ⁻²⁸ T ^{-1.6} M = N ₂ k _r = 6.1 x 10 ⁻³ T ^{-1.6} exp(-113,200/T) cm ³ molecule ⁻¹ s ⁻¹ M = N ₂ | 1.5 |
| | Taylor (1975) review | 2000-10000 | k _f = 7.6 x 10 ⁻³² T ^{-1/2} M = N ₂ k _f = 3.0 x 10 ⁻³² T ^{-1/2} M = N ₂ , N ₂ k _f = 6.5 x 10 ⁻²⁷ T ^{-3/2} M = N | 3 |

This evaluation accepts the recommendations in the review of Baulch et al (1973)

REFERENCES

- Baulch, D. L., Drysdale, D. D., and Horne, D. G., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 2: Homogeneous Gas Phase Reactions of the F₂-N₂-O₂ System," (Butterworths, London, 1973)
- Taylor, R. L., "High Temperature Reactions of Air" pages 5-154 to 5-157 in "The Natural Stratosphere of 1974" Climatic Impact Assessment Program Monograph 1, DDT-TST-75-51, Department of Transportation, Washington D.C., September 1975

P. F. Hampson
May 1976

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No | Reaction/Reference | Temp. Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncert. Factor at 298K, notes |
|------|---|------------------|--|----------------------------------|
| 8.9 | N + NO → N ₂ + O (f) | | ΔH (298) = -314 kJ/mol | |
| 1,12 | N + N ₂ → N ₃ (r) | | | |
| | NASA (1979) eval | 200-300 | k _f = 3.4 x 10 ⁻¹¹ exp((0±100)/T) | 1.4 |
| | CMDATA (1979) eval | 200-400 | k _f = 3.4 x 10 ⁻¹¹ exp((0±100)/T) | 1.4 |
| | Lee, et al (1978) | 196-400 | k _f = 3.4 x 10 ⁻¹¹ | |
| | Clyne, McDermid (1975) | 298-670 | k _f = 8.2 x 10 ⁻¹¹ exp(-410/T) | |
| | Baulch, et al (1973) review | 2000-5000 | k _r = 1.3 x 10 ⁻¹⁰ exp(-38000/T) | |
| | Taylor (1975) review | 2000-10000 | k _f = 2.7 x 10 ⁻¹¹ | |

Recommendation is based on the results of Lee et al (1978) and is significantly different from that in NASA RP-1010 which accepted the results of Clyne and McDermid (1975). Based on our critical re-examination of the high temperature data reported by those authors, their derived temperature dependence is rejected. Independent confirmation is needed

REFERENCES

- Baulch, D. L., Drysdale, D. D., and Horne, D. G., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 2: Homogeneous Gas Phase Reactions of the H₂-N₂-O₂ System," (Butterworths, London, 1973)
- Clyne, M. A. A., and McDermid, I. O., "Mass Spectrometric Determinations of Rates of Elementary Reactions of N₃ and of N₂ with Ground State N₂ Atoms," J. Chem. Soc., Faraday Trans 1 **71**, 2189-2208 (1975)
- CMDATA (1979) - Recommendations of the CMDATA Task Group on Chemical Kinetics to be published in the Journal of Physical and Chemical Reference Data
- Lee, J. H., Michael, J. V., Payne, W. A., and Stief, L. J., "Absolute Rate of the Reaction of N(⁴S) with N₂ from 196-400 K with DF-RF Techniques," J. Chem. Phys. **65**, 3069-3076 (1975)
- NASA RP-1010, "Chlorofluoromethanes and the Stratosphere" by D. Hudson, Editor, August 1977 This reference contains the NASA (1977) rate constant recommendations.

NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA SP 1049 "The Stratosphere: Present and Future," P. D. Hudson and E. L. Reed, Editors, Dec. 1979 (report of the June 1979 Waples Ferry Workshop).

Taylor, R. L. "High Temperature Reactions of Air" pages 5-154 to 5-157 in "The Natural Stratosphere of 1974" Climatic Impact Assessment Program Monograph 1, DGI-TST-75-51, Department of Transportation, Washington D.C., September 1975

R. P. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Uncert Factor
at 298K, notes

Reaction Rate Constant
k/cm³molecule⁻¹s⁻¹

Temp.
Range/K

Reaction/Reference

No

1-25
1-5

ΔH (298) = -175 kJ/mol

200-300
298
298

M + NO₂ → N₂O + O
NASA (1979) eval
CDDATA (1979) eval
Clyne, McDermid (1975)

2.1 x 10⁻¹¹
1.4 x 10⁻¹²
1.4 x 10⁻¹²

Accepts the 298 K results of Clyne and McDermid (1975)--both the value of the rate constant and the identity of the products. A pre-exponential factor of 2 x 10⁻¹¹ was chosen as a reasonable estimate and the temperature dependence was derived from a fit to the room temperature rate constant. Clearly, temperature dependent studies are needed

REFERENCES

Clyne, M. A. A., and McDermid, I. C. "Mass Spectrometric Determinations of Rates of Elementary Reactions of NO and of NO₂ with Ground State N⁴S Atoms." J. Chem. Soc., Faraday Trans. I **71**, 2189-2208 (1975)

CDDATA(1979). Recommendations of the CDDATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.

NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," R. D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the June 1979 Harpers Ferry Workshop).

P. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No | Reaction/Reference | Temp. Range/K | Reaction Rate Constant $k/\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ | Uncert. Factor at 298K, notes |
|------|--|------------------|--|----------------------------------|
| 0.19 | $\text{H} + \text{H}_2 \rightarrow \text{H}_2 + \text{H}$ Baulch, et al (1973) review | 300 | $\Delta H (298) = -203 \text{ kJ/mol}$ 5.3×10^{-11} (a) Based on $k/k(\text{H} + \text{H}_2 \rightarrow \text{H}_2 + \text{H}) = 1.4$ | 2 |

This evaluation accepts the recommendation in the review of Baulch et al (1973)

REFERENCES

Baulch, D. L., Drysdale, D. D., and Horne, D. G., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 2: Homogeneous Gas Phase Reactions of the H_2 - N_2 - O_2 System," (Butterworths, London, 1973)

P. F. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No | Reaction/Reference | Temp- Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncert Factor at 298K, notes |
|------|--|------------------|--|---------------------------------|
| 8.27 | N + SO → NO + S Baulch, et al (1976) review | | AR (298) = -110 kJ/mol no recommendation | |

See the review of Baulch et al (1976) for a discussion of reported results. However, because of an insufficient data base, no recommendation can be made

REFERENCES

Baulch, D. L., Drysdale, D. D., Duxbury, J., and Grant, S. J., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 3: Homogeneous Gas Phase Reactions of the O₂-O₃ System, the CO-O₂-H₂ System, and of Sulphur-Containing Species," (Butterworths, London, 1976)

R. F. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No | Reaction/Reference | Temp. Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncert Factor at 298K, notes |
|------|---|------------------|--|---------------------------------|
| 8.20 | N + SO ₃ → NO + SO ₂ Baulch, et al (1976) review | | ΔH (298) = -283 kJ/mol no recommendation | |

See the review of Baulch et al (1976) for a discussion of reported results. However, because of an insufficient data base, no recommendation can be made

REFERENCES

Baulch, D. L., Drysdale, D. D., Duxbury, J., and Grant, S. J., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 3: Homogeneous Gas Phase Reactions of the O₂-C₃ System, the C₆-O₂-H₂ System, and of Sulphur-Containing Species," (Butterworths, London, 1976)

R. F. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No | Reaction/Reference | Temp. Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncert Factor at 298K, notes |
|------|---|------------------|--|---------------------------------|
| 8.37 | H + OClO - NO + ClO Watson (1977) review | 298 | ΔH (298) = -377 kJ/mol k = 6 x 10 ⁻¹³ | preliminary value |

No recommendation

REFERENCES

Watson, B. To. "Rate Constants for Reactions of ClO₂ of Atmospheric Interest," J. Phys. Chem. Ref. Data 6, 871-918 (1977)
 R. F. Hampson
 May 1978

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No | Reaction/Reference | Temp. Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncert. Factor at 298K, notes |
|-----|---|------------------|--|----------------------------------|
| 9.9 | $\text{NO} + \text{NO} \rightarrow \text{N} + \text{NO}_2$ Baulch, et al (1973) review | | $\Delta H (298) = 325 \text{ kJ/mol}$ Endothermic. Unimportant compared to $\text{NO} + \text{NO} \rightarrow \text{N}_2\text{O} + \text{O}$ | |

There is no evidence for this reaction

REFERENCES

Baulch, D. L., Drysdale, D. D., and Horne, D. G., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 2: Homogeneous Gas Phase Reactions of the H_2 - N_2 - O_2 System," (Butterworths, London, 1973)

D. F. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No | Reaction/Reference | Temp- Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncert Factor at 298K, notes |
|----------------------|--|------------------|--|---------------------------------|
| 9.1 ¹ .22 | NO + NO ₂ + H ₂ O → 2HNO ₂ (z) 2HNO ₂ → NO + NO ₂ + H ₂ O (r) Chan, et al (1976) | | ΔH (298) = - 41 kJ/mol | |
| | | 296 | k _f = 6.0 x 10 ⁻³⁸ cm ⁶ molecule ⁻² s ⁻¹ k _r = 9.5 x 10 ⁻¹⁹ cm ³ molecule ⁻¹ s ⁻¹ | |
| | Kaiser, Wu (1977) | 300 | k _f ± 4.4 x 10 ⁻⁴⁰ cm ⁶ molecule ⁻² s ⁻¹ k _r ± 1 x 10 ⁻²⁰ cm ³ molecule ⁻¹ s ⁻¹ | |
| | Hampson, et al (1973) review | 300 | Reviewed earlier work, probably heterogeneous | |

No recommendation

REFERENCES

- Chan, W. E., Nordstrom, R. J., Calvert, J. G., and Shaw, J. H., "An IRFTS Spectroscopic Study of the Kinetics and the Mechanism of the Reactions in the Gaseous System. HONO, NO, NO₂, H₂O," Chem. Phys. Lett. **37**, 441-446 (1976)
- Hampson, R. F., (editor), "Survey of Photochemical and Rate Data for Twenty-Eight Reactions of Interest in Atmospheric Chemistry," J. Phys. Chem. Ref. Data **2**, No. 2 pgs. 267-312 (1973). These are revised versions of data sheets originally distributed as NBS Reports 10692 and 10829.
- Kaiser, E. W., and Wu, C. H., "A Kinetic Study of the Gas Phase Formation and Decomposition Reactions of Nitrous Acid," J. Phys. Chem. **81**, 1701-1706 (1977)

W. F. Hampson
 May 1978

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No | Reaction/Reference | Temp. Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncert. Factor at 298K, notes |
|-------|--|------------------|--|----------------------------------|
| 9,11 | NO + NO ₃ → 2NO ₂ (r) | | ΔH (298) = - 95 kJ/mol | |
| 10,10 | NO ₂ + NO ₂ → NO + NO ₃ (r) | | | |
| | NASA (1979) eval | 298 | k _f = 2 x 10 ⁻¹¹ | 3 |
| | CODATA (1979) eval | 298 | k _f = 2 x 10 ⁻¹¹ | 3 |
| | Graham, Johnston (1978) | 300 | k _f = (1.9 ± 0.4) x 10 ⁻¹¹ | |
| | Baulch, et al (1973) review | 300 | k _f ~ 2 x 10 ⁻¹¹ k _r no recommendation | |

This recommendation accepts the value reported by Graham and Johnston (1978) with increased error limits

REFERENCES

- Baulch, D. L., Drysdale, D. D., and Horne, D. G., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 2: Homogeneous Gas Phase Reactions of the H₂-H₂-O₂ System," (Butterworths, London, 1973)
- CODATA(1979). Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.
- Graham, R. A., and Johnston, R. S., "The Photochemistry of NO₃ and the Kinetics of the H₂O₂-O₃ System," J. Phys. Chem. **82**, 254-268 (1978)
- NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future,"
- R. D. Hudson and R. L. Reed, Editors, Dec. 1979 (report of the June 1979 Harpers Ferry Workshop).
- R. F. Hampson
 June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No | Reaction/Reference | Temp- Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncert Factor at 298K, notes |
|------|--------------------------------|------------------|--|---------------------------------|
| 9.15 | N ₆ + NH → products | | | |
| | Hansen, et al (1976) | 300 | (4.7 ± 1.2) × 10 ⁻¹¹ | |
| | Gordon, et al (1971) | 300 | 3.8 × 10 ⁻¹¹ | |
| | Mulvihill, Phillips (1975) | 1500 | N ₂ + O + H identified as products of major rxn channel | |

No recommendation

REFERENCES

- Hansen, I., Hoisinghaus, L., Zetzsch, C., and Stuhl, F., "Detection of NH(X¹Σ⁺) by Resonance Fluorescence in the Pulsed Vacuum UV Photolysis of NH₃ and Its Application to Reactions of NH Radicals," Chem. Phys. Lett. **42**, 370-372 (1976)
- Gordon, R., Mulac, W., and Mangia, F., "Pulse Radiolysis of Ammonia Gas: II. Rate of Disappearance of the NH₂(X²B₁) Radical," J. Phys. Chem. **75**, 2087-2093 (1971)
- Mulvihill, J. M., and Phillips, L. F., "Products of Reaction of NH with N₆," Chem. Phys. Lett. **25**, 327-329 (1975)
- R. F. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| Reaction/Reference | Temp. Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncert. Factor at 298K, notes |
|---|---------------|--|----------------------------------|
| 9.16 | | | |
| NO + NH ₂ → N ₂ + H ₂ O ^a | | ΔH (298) = -517 kJ/mol | |
| Hancock, et al (1975) | 298 | 2.1 × 10 ⁻¹¹ | 1-5 |
| Lesclaux, et al (1975) | 300 | 1.8 × 10 ⁻¹¹ | (a) |
| | | (a) T ^{-1.25} dependence observed 300-500K | |
| Gehring, et al (1973) | 300 | 8 × 10 ⁻¹² | |
| Gordon, et al (1971) | 300 | 2.7 × 10 ⁻¹¹ | |

This evaluation accepts the results of Hancock et al (1975) which are confirmed by the results of Lesclaux et al (1975)

REFERENCES

- Gehring, M., Heyermann, K., Schacke, K., and Wolfrum, J., "Direct Studies of Some Elementary Steps for the Formation and Destruction of Nitric Oxide in the H-N-O System," Sympo Combust. 14th (Combustion Institute, Pittsburgh, 1973) 99-105
- Gordon, S., Mulac, W., and Nangia, P., "Pulse Radiolysis of Ammonia Gas: II. Rate of Disappearance of the NH₂(¹Σ_g⁺) Radical," J. Phys. Chem. **75**, 2087-2093 (1971)
- Hancock, G., Lange, W., Lenzi, M., and Welge, K. H., "Laser Fluorescence of NH₂ and Rate Constant Measurement of NH₂ + NO," Chem Phys. Lett. **33**, 168-172 (1975)
- Lesclaux, P., van Khe, P., Dezauxier, P., and Soullignac, J. C., "Flash Photolysis Studies of the Reaction of NH₂ Radicals with NO," Chem. Phys. Lett. **35**, 493-497 (1975)
- P. F. Hampson
May 1976

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No | Reaction/Reference | Temp Range/K | Reaction Rate Constant $k/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$ | Uncert Factor at 298K, notes |
|-------|--|--------------|--|---------------------------------|
| 9.12M | $\text{NO} + \text{H} + \text{M} \rightarrow \text{HNO} + \text{M} (z)$ | | $\Delta H (298) = -209 \text{ kJ/mol}$ | |
| 24. M | $\text{HNO} + \text{H} + \text{M} \rightarrow \text{H}_2\text{O} + \text{M} (r)$ | | | |
| | Baulch, et al (1973) review | 230-700 | $k_f = 1.5 \times 10^{-32} \exp(300/T) \text{ cm}^6\text{molecule}^{-2}\text{s}^{-1}$ $k_r = k_f/K_{eq} = 5 \times 10^{-8} \exp(-24500/T) \text{ M} = \text{H}_2$ | 1.5 |
| | Atkinson, Cvetanovic (1973) | 286-390 | $k_f = 2.5 \times 10^{-32} \exp(270/T) \text{ M} = \text{H}_2$ | |
| | Allen, Moortgat (1973) | 180-300 | $k_f = 5.6 \times 10^{-33} \exp(375/T), \text{ M} = \text{Ar}$ | |

This evaluation accepts the recommendations in the review of Baulch et al (1973)

REFERENCES

- Allen, E. P., and Moortgat, G. L., "Kinetic Studies of the Termolecular Reactions of Hydrogen Atoms with Nitric Oxide and with Molecular Oxygen," Third Int. Symp. Gas Kinetics, Brussels (1973), Abstract D1
- Atkinson, R., and Cvetanovic, R. J., "Determination of the Rates of Hydrogen Atom Reaction with NO by a Modulation Technique," Can. J. Chem. 51, 370-372 (1973)
- Baulch, D. L., Drysdale, D. D., and Horne, D. G., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 2: Homogeneous Gas Phase Reactions of the $\text{H}_2\text{-N}_2\text{-O}_2$ System," (Butterworths, London, 1973)

E. F. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No | Reaction/Reference | Temp. Range/K | Reaction Rate Constant k/cm ³ molecule ⁻² s ⁻¹ | Uncert. Factor at 298K, notes |
|---------------------------------|---|------------------|--|----------------------------------|
| 9.10H | N ₂ + NO(·M) → HNO ₂ (·M) | | ΔH (298) = -209 kJ/mol | |
| NASA (1979) eval | | 200-300 | k = (6.7±1.2) × 10 ⁻³¹ (T/300) ^{-3.3±1} , M = N ₂ | |
| | | | k _∞ = (3.0±1.5) × 10 ⁻¹¹ (T/300) ^{-1±1} cm ³ molecule ⁻¹ s ⁻¹ | |
| CDATA (1979) eval | | 220-440 | k = 6.5 × 10 ⁻³¹ (T/300) ^{-2.4} , M = N ₂ | 1.3 |
| | | | k _∞ = 1.0 × 10 ⁻¹¹ cm ³ molecule ⁻¹ s ⁻¹ | 1.6 |
| Baulch, et al (1973) review | | 273-395 300 | 2.2 × 10 ⁻³² exp(-1110/T) M = He 2 × 10 ⁻¹² cm ³ molecule ⁻¹ s ⁻¹ | 1.6 2 |
| Anderson, et al, (1974) | | 295, 439 | (2d order high pressure limit) 5.0 ± 1.2 × 10 ⁻³¹ × (295/T) ^{2.4} M = N ₂ | |
| Howard, Evensen (1974) | | 296 | Relative efficiencies: N ₂ (1.0), Ar(0.56), He(-.51) | |
| Cox (1974) | | 254 | 7.2 ± 1.2 × 10 ⁻³¹ M = N ₂ Relative efficiencies: N ₂ (1.0), Ar(0.56), He(-.51) k/(H ₂ + C ₆) = 40 ± 7 k = 1.2 × 10 ⁻¹¹ cm ³ molecule ⁻¹ s ⁻¹ | (a) |
| | | | (a) 2nd order rate constant, [M] = 1 atm N ₂ + C ₆ ; k _{ref} = 3 × 10 ⁻¹³ , this survey | |
| Barris, Wayne (1975) | | 300 | 7 ± 2 × 10 ⁻³¹ M = Ar 15 ± 5 × 10 ⁻³¹ , M = N ₂ | |
| Gordon, Mulec (1975) | | 435 | 7.5 ± 0.3 × 10 ⁻¹² cm ³ molecule ⁻¹ s ⁻¹ (2nd order rate constant at 1 atm H ₂ O vapor) | |
| Atkinson, Hensen, Pitts (1975a) | | 256 | 4.54 ± 0.5 × 10 ⁻¹³ M = 25 Torr N ₂ | (b) |
| Cox, Derwent, Holt (1976) | | 298 | (b) also data for M = Ar at 25-655 torr 1.17 × 10 ⁻¹¹ M = 1 atm N ₂ + O ₂ | (c) |
| | | | (c) relative to k(H ₂ + H ₂) = 7 × 10 ⁻¹⁵ | |
| Overend, et al (1976) | | 295 | 0.556 ± 0.05 × 10 ⁻¹² M = 25 torr N ₂ | |
| Sie, et al (1976b) | | 298 | 6.09 ± 0.68 × 10 ⁻¹² M = 770 torr N ₂ k/k _{ref} = 16.1 at 95 torr and = 22 at 406 and 768 torr total pressure, mostly H ₂ where ref rxn is H ₂ + C ₆ - C ₆ + H | |

REFERENCES

- Anderson, J. G., Margitan, J. J., and Kaufman, F., "Gas Phase Recombination of OH with NO and NO₂," J. Chem. Phys., **59**, 3310-3317 (1974)
- Atkinson, R., Hensen, D. A., and Pitts, J. N., Jr., "Rate Constants for the Reaction of the CH Radical with H₂ and NO (M = Ar and N₂)," J. Chem. Phys., **62**, 3284-3288 (1975a)

- Baulch, D. L., Drysdale, D. L., and Horne, D. G., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 2: Homogeneous Gas Phase Reactions of the H_2 - H_2O - O_2 System," (Butterworths, London, 1973) CODATA(1979). Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.
- Cox, R. A., "The Photolysis of Nitrous Acid in the Presence of Carbon Monoxide and Sulphur Dioxide," *J. Photochem. E.* 291-304 (1974)
- Cox, R. A., Derwent, R. G., and Holt, F. W., "Relative Rate Constants for the Reactions of OH Radicals with H_2 , CH_4 , CO , HC and $HONC$ at Atmospheric Pressure and 296 K," *J. Chem. Soc., Faraday Trans. I* 22, 2031-2043 (1976)
- Gordon, S., and Mulas, W. A., "Reaction of the $OH(X^2\Delta)$ Radical Produced by the Pulse Radiolysis of Water Vapor," *Int. J. Chem. Kinet., Symp. No. 1*, 289-295 (1975)
- Harrie, G. W., and Wayne, R. P., "Reaction of Hydroxyl Radicals with NO , NO_2 and SO_2 ," *J. Chem. Soc., Faraday Trans. I* 21, 610-617 (1975)
- Howard, C. J., and Evenson, E. M., "Laser Magnetic Resonance Study of the Gas Phase Reactions of OH with CO , NO , and NO_2 ," *J. Chem. Phys.* 51, 1943-1952 (1974)
- NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," R. D. Hudson and E. L. Reed, Editors, Deco 1979 (report of the June 1975 Harpers Ferry Workshop).
- Overend, R., Paraskevopoulos, G., and Black, C., "Rates of OH Radicals Reactions. II. The Combination Reaction $OH + NO + M$," *J. Chem. Phys.* 54, 4149-4154 (1976)
- Sie, R. K. T., Simonsitis, R., and Heicklen, J., "The Reaction of OH with NO ," *Int. J. Chem. Kinet.* 5, 99-106 (1976b)
- R. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Uncertainty Factor
at 298K, notes

| No. | Reaction/Reference | Tempo Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncertainty Factor at 298K, notes |
|------|---|------------------|--|--------------------------------------|
| 9.20 | NO + NO ₂ → NO ₂ + NO | | | |
| | NASA (1979) eval | 200-300 | 4.3 x 10 ⁻¹² exp((200±200)/T) | 10 ² |
| | CODATA (1979) eval | 230-425 | 4.3 x 10 ⁻¹² exp((200±200)/T) | 10 ² |
| | Zahniser, Howard (1978) | 230-400 | 3.3 x 10 ⁻¹² exp(254/T) | |
| | Leu (1979) | 270-425 | 5.7 x 10 ⁻¹² exp(130/T) | |
| | Margitan, Anderson (1978) | 258 | 8.0 x 10 ⁻¹² | |
| | Kaufman, Reimann (1972) | 298 | 7.5 x 10 ⁻¹² | |
| | Burrows, et al (1978) | 298 | 8.2 x 10 ⁻¹² | |
| | Howard, Evenson (1977) | 296 | (8.1 ± 1.5) x 10 ⁻¹² | |
| | Hack, et al (1975) | 258-670 | 2.0 x 10 ⁻¹¹ exp(-1200/T) | |
| | Simoneitis, Reichlen (1977) | 245-328 | k/(k _{ref}) ^{0.5} = 6.4 x 10 ⁻⁶ exp(-700/T) | (a) |
| | | | (a) ref rxn: 2H ₂ → H ₂ O ₂ + O ₂ | |
| | Cox, Derwent (1975) | 256 | 1.2 x 10 ⁻¹² | |
| | Payne, Stiet, Davis (1973) | 300 | 3 x 10 ⁻¹³ | |
| | Glanzer, Troe (1975) | 1350-1700 | 7.5 x 10 ⁻¹² | |

The recommendation is based on Zahniser and Howard (1978) and Leu (1979) and the room temperature determinations of Margitan and Anderson (1978) and Kaufman and Reimann (1978) and the ratio determination by Burrows et al (1978) relative to OH + H₂O₂. The agreement is excellent

REFERENCES

Burrows, J. P., Cliff, D. I., Harris, G. W., Thrush, B. A.,
 and Wilkinson, J. P. I., paper presented at WMS
 Symposium on Ozone, Toronto, June (1978)

- CODATA(1979). Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.
- Cox, R. A., and Durrant, R. G. "Kinetics of the Reaction of H_2 with Nitric Oxide and Nitrogen Dioxide." *J. Photochem. A*, 139-153 (1975)
- Glanzer, K., and Troe, J. "H₂ Formation in Shock Heated HNO_3 - H_2 Mixtures," *Ber. Bunsenges. Phys. Chem.* **79**, 465-469 (1975)
- Hack, M., Meyer, R., and Wagner, H. G. "The Reaction $\text{H}_2 + \text{H}_2 - \text{H}_2 + \text{H}_2$ with CH_4 and $\text{H}_2\text{O} - \text{H}_2 + \text{H}_2$ as an H_2 - Source," *Int. J. Chem. Kinet.* **5**, 329-339 (1973)
- Howard, C. J., and Evenson, K. M., "Kinetics of the Reaction of H_2 with NO ," *Geophys. Res. Lett.* **4**, 437-440 (1977)
- Kaufman, F., and Reimann, R. 1978, paper presented at 13th Informal Conference on Photochemistry, Clearwater Beach, Florida, January, 1978
- Lou, M.-T., "Rate Constant for the Reaction $\text{H}_2 + \text{NO} \rightarrow \text{OH} + \text{NO}_2$," *J. Chem. Phys.* **70**, 1662-1666 (1979)
- Margitan, J. J., and Anderson, J. G., 1978, paper presented at 13th Informal Conference on Photochemistry, Clearwater Beach, Florida, January, 1978
- NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," by D. Hudson and E. L. Peed, Editors, Dec. 1979 (report of the June 1979 Harpers Ferry Workshop).
- Payne, W. A., Stief, L. J., and Davis, D. D., "A Kinetics Study of the Reaction of H_2 with SO_2 and NO ," *J. Amer. Chem. Soc.* **95**, 7614-7619 (1973)
- Simonaitis, P., and Heicklen, J., "The Temperature Dependence of the Reactions of H_2 with NO and NO_2 ," *Int. J. Chem. Kinet.* **10**, 67-87 (1978)
- Zahniser, W. S., and Howard, C. J., Manuscript to be published, 1979.
- P. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No | Reaction/Reference | Temp. Range/K | Reaction Rate Constant $k/cm^3 \text{ molecule}^{-1} s^{-1}$ | Uncert. Factor at 298K, notes |
|------|---|------------------|--|----------------------------------|
| 9.23 | $NO + H_2O_2 \rightarrow NO_2 + H_2O$ Hampson, et al (1973) review | 300 500 | $\Delta H (298) = 6 \text{ kJ/mol}$ $< 5 \times 10^{-20}$ $\sim 2 \times 10^{-20}$ | |
| | Gray, et al (1972) | 300 | $< 5 \times 10^{-20}$ | |

This evaluation accepts the recommendations in the review of Hampson et al (1973)

REFERENCES

Gray, D., Liss, E., and Reichlen, J., "The Reaction of Hydrogen Peroxide with Nitrogen Dioxide and Nitric Oxide," J. Phys. Chem. **76**, 1919-1924 (1972)

Hampson, R. F., (editor), "Survey of Photochemical and Rate Data for Twenty-Eight Reactions of Interest in Atmospheric Chemistry," J. Phys. Chem. Ref. Data **2**, No. 2, pgs. 267-312 (1973). These are revised versions of data sheets originally distributed as NBS Reports 10692 and 10828.

R. F. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Uncert Factor
at 298K, notes

| No | Reaction/Reference | Temp. Range/K | Reaction Rate Constant k/cm ⁶ molecule ⁻² s ⁻¹ | Uncert Factor at 298K, notes |
|-------|--|------------------|---|---------------------------------|
| 9,35M | NO + Cl + M → ClNO + M NASA (1979) eval | 200-300 | ΔH (298) = -160 kJ/mol k = (9±2) × 10 ⁻³² (T/300) ^{-1.8±0.5} , M = N ₂ | |
| | Lee, et al (1978a) | 200-400 | k = 1.18 × 10 ⁻³² exp(532/T), M = N ₂ k = 7.15 × 10 ⁻³² (T/300) ^{-1.91} , M = N ₂ | |
| | Watson (1977) review | 293 | k = 1.1 × 10 ⁻³¹ , M = N ₂ | |

REFERENCES

- Lee, J. R., Michael, J. V., Payne, W. A. Jr., and Stief, L. J.,
"The Temperature Dependence of the Rate Constant for
Cl + NO + N₂ → NOCl + N₂," J. Chem. Phys. **68**, 5410-5413
(1978a)
- NASA (1979). Recommendations of the NASA Panel for Data Evaluation,
published in NASA EP 1049 "The Stratosphere: Present and Future,"
R. D. Hudson and E. L. Reed, Editors, Dec. 1979 (report of the
June 1975 Harpers Ferry Workshop).
- Watson, R. L., "Rate Constants for Reactions of ClO₂ of Atmospheric
Interest," J. Phys. Chem. Ref. Data **6**, 871-918 (1977)
- R. P. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Temp. Range/K | Reaction Rate Constant k/cm ³ molecule ⁻² s ⁻¹ | Uncertainty Factor at 298K, notes |
|-------|--|------------------|--|--------------------------------------|
| 9.38F | NO + F + M → FNO + M NASA (1979) eval | 200-300 | k = (6.6±3.3) × 10 ⁻³² (T/300) ⁻¹ , M = N ₂ | |

Estimated values; no data

REFERENCES

NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," B. D. Hudson and E. I. Reed, Editors, Dec 1975 (report of the June 1975 Harpers Ferry Workshop).

B. F. Bumpson
 June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No | Reaction/Reference | Temp. Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncert. Factor at 298K, notes |
|------|--|---|--|---|
| 9.36 | NO + ClO → NO ₂ + Cl NASA (1979) eval CODATA (1979) eval Leu, DeMore (1978) Watson, Ray (1979) Clyne, Watson (1974a) Watson (1977) review Zahniser, Kaufman (1977) | 200-300 227-415 227-415 298 298 220-298 230-298 | ΔH (298) = - 38 kJ/mol 7.8 x 10 ⁻¹² exp((250±100)/T) 8.9 x 10 ⁻¹² exp((210±100)/T) 5.7 x 10 ⁻¹² exp(296/T) 1.75 x 10 ⁻¹¹ 1.7 x 10 ⁻¹¹ 8 x 10 ⁻¹² exp(250/T) k/k _{ref} = (0.52 ± 0.05)exp(373 ± 23/T) (a) k _{ref} = k(Cl + O ₃) | 1-25 1-25 (a) |

Changed from NASA 1010. The results of the three mass spectrometric studies (Clyne and Watson (1974a), Leu and DeMore (1978) and Watson and Ray (1979)) are in excellent agreement at 298 K. However, unless it can be shown that the value reported by Zahniser and Kaufman (1977) is in error, the preferred value at 298 K is taken to be the mean of all of these results. The magnitude of the temperature dependence reported by Leu and DeMore, and Zahniser and Kaufman is in good agreement. The Arrhenius expression was derived by taking the average of the two values of E/N and the pre-exponential A-factor was adjusted so that the expression yielded the preferred value of 1.8 x 10⁻¹¹ at 298 K

REFERENCES

CODATA(1979). Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.

Clyne, M. A. A., and Watson, R. T., "Kinetic Studies of Diatomic Free Radicals using Mass Spectrometry Part 2. Rapid Bimolecular Reactions Involving the ClO X²Π Radical," J. Chem. Soc., Faraday Trans. 1 70, 2250-2259 (1974a)

Leu, M. T., and DeMore, W. B., "Rate Constant for the Reaction ClO + NO → Cl + NO₂," J. Phys. Chem. 82, 2049-2052 (1978)

NASA RP-1010, "Chlorofluoromethanes and the Stratosphere" R. D. Hudson, Editor, August 1977 This reference contains the NASA (1977) rate constant recommendations.

NASA (1979), Recommendations of the NASA Panel for Data Evaluation,
published in NASA RP 1049 "The Stratosphere: Present and Future,"
R. B. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the
June 1979 Harpers Ferry Workshop).
Watson, R. T., "Rate Constants for Reactions of ClO_2 of Atmospheric
Interest," J. Phys. Chem. Ref. Data 6, 871-918 (1977)
Watson, R. T., and Ray, G., 1979, Manuscript in preparation
Zahnleer, M. S., and Kaufman, F., "Kinetics of the Reactions of ClO with
 O and with NO ," J. Chem. Phys. 66, 3673-3681 (1977)
R. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY
 PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Uncertainty Factor
 at 298K, notes

Reaction/Reference

Tempo
 Range/K

Reaction Rate Constant
 $\text{k/cm}^3\text{-molecule}^{-1}\text{s}^{-1}$

No.

| | | | |
|--------|--|---------------------------------------|---|
| 9.36Br | $\text{NO} + \text{BrO} \rightarrow \text{NO}_2 + \text{Br}$ | $\Delta H (298) = -71 \text{ kJ/mol}$ | |
| | NASA (1979) eval | 200-300 | $8.7 \times 10^{-12} \exp((265 \pm 130)/T)$ |
| | CODATA (1979) eval | 224-425 | $8.7 \times 10^{-12} \exp((260 \pm 100)/T)$ |
| | Leu (1979) | 230-425 | $7.1 \times 10^{-12} \exp(296/T)$ |
| | Watson, Sander, Yung (1979) | 224-396 | $1.3 \times 10^{-11} \exp(181/T)$ |
| | Pay, Watson (1979) | 252 | 2.3×10^{-11} |
| | Clyne, Watson (1975) | 258 | 2.2×10^{-11} |
| | Clyne, Cruse (1970) | 258 | 2.5×10^{-12} |

Changed from NASA 1010 due to new data. The results of the three low pressure mass spectrometric studies (Clyne and Watson (1975), Ray and Watson (1979) and Leu (1979)) and the high pressure uv absorption study (Watson, Sander and Yung (1979), which all used pseudo first-order conditions, are in excellent agreement at 298 K, and are thought to be much more reliable than the earlier low pressure uv absorption (Clyne and Cruse (1970)). The results of the two temperature dependence studies are in good agreement and both show a small negative temperature dependence. The preferred Arrhenius expression was derived from a least squares fit to all the data reported in the four recent studies. By combining the data reported by Watson, Sander and Yung (1979) with that from the three mass spectrometric studies, it can be shown that this reaction does not exhibit any observable pressure dependence between 1 and 700 torr total pressure. The temperature dependence of k for the analogous ClO and HO_2 reactions are also negative, and are similar in magnitude.

REFERENCES

- Clyne, W. A. A., and Cruse, H. W., "Rates of Elementary Reactions Involving the BrO ($\text{X}^2\Pi$) and IO ($\text{X}^2\Pi$) Radicals, Part 2. Reactions of the BrO and IO Radicals," *Trans. Faraday Soc.* **66**, 2227-2236 (1970)
- Clyne, W. A. A., and Watson, R. T., "Kinetics Studies for Diatomic Free Radicals using Mass Spectrometry Part 3 - Elementary Reactions Involving BrO ($\text{X}^2\Pi$) Radicals," *J. Chem. Soc., Faraday Trans. 1* **71**, 336-350 (1975)
- CODATA (1979). Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.

Iou, M-To. "Rate Constant for the Reaction $\text{Br} \cdot + \text{NO} \rightarrow \text{Br} + \text{NO}_2$,"
Chem. Phys. Lett. 51, 275-279 (1979)
NASA RP-1010. "Chlorofluoromethanes and the Stratosphere"
R. D. Hudson, Editor, August 1977 This reference contains
the NASA (1977) rate constant recommendations.
NASA (1979). Recommendations of the NASA Panel for Data Evaluation,
published in NASA RP 1049 "The Stratosphere: Present and Future,"
R. D. Hudson and E. L. Reed, Editors, Dec. 1979 (report of the
June 1979 Harpers Ferry Workshop).
Ray, G., and Watson, R. L., 1979, Manuscript in preparation
Watson, R. L., Sander, S. P., and Yung, Y. L., 1979, Manuscript in
preparation
V. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Uncert. Factor
at 250K, notes

Reaction/Reference Temp.
Range/K Reaction Rate Constant
k/cm³molecule⁻¹s⁻¹

No.

9.36F NO + Fd → NO₂ + F
NASA (1979) eval 200-300 2 × 10⁻¹¹ exp((0.250)/T)
CODATA (1975) eval 250 2 × 10⁻¹¹

ΔH (298) = -239 kJ/mol

3
3

See entry. Although there have been no experimental studies of this reaction, it has been used as a rapid titration reaction by Clyne and Watson (1974). The estimate is probably accurate to within a factor of 3, and is based upon the assumption that the reactivity of Fd is similar to that of ClO and BrO. The experimentally determined rate constants for ClO and BrO at -250 K are 1.6 × 10⁻¹¹ and 2.1 × 10⁻¹¹, respectively (this evaluation). The temperature dependence of k is expected to be small for such a radical reaction. The temperature dependences of k for the analogous ClO and BrO reactions have been reported to be negative with E/R values of -200 K (Zahniser and Kaufman (1977) and -300 K (Leu and Demore (1978) for ClO, and -296 K (Leu (1979) and -180 K (Watson and Sander (1978) for BrO.

REFERENCES

- Clyne, M. A. and Watson, R. T., "Kinetic Studies of Diatomic Free Radicals using Mass Spectrometry Part I: System Description and Applications to F Atoms and F₂ Radicals," J. Chem. Soc., Faraday Trans. 1 **70**, 1169-1123 (1974)
- CODATA (1979), Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.
- Leu, M.-T., "Rate Constant for the Reaction BrO + NO → Br + NO₂," Chem. Phys. Lett. **51**, 275-279 (1979)
- Leu, M. T., and Demore, R. B., "Rate Constant for the Reaction ClO + NO → Cl + NO₂," J. Phys. Chem. **82**, 2049-2052 (1978)
- NASA (1979), Recommendations of the NASA Panel for Late Evaluation, published in NASA SP 1049 "The Stratosphere: Present and Future," B. D. Hudson and E. I. Reed, Editors, Dec. 1975 (report of the June 1975 Harpers Ferry Workshop).

Nelson, E. T., and Sander, E. P., 1978, Manuscript in preparation.

Zahnleer, M. S., and Kaufman, F., "Kinetics of the Reactions of ClO with O and with H_2 ," J. Chem. Phys. 66, 3672-3681 (1977)

E. P. Hanson
June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No | Reaction/Reference | Temp. Range/K | Reaction Rate Constant $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | Uncert Factor at 298K, notes |
|------|--|------------------|--|---------------------------------|
| 9.37 | $\text{NO} + \text{OClO} \rightarrow \text{NO}_2 + \text{ClO}$ NASA (1979) eval Bemand, Clyne, Watson (1973) | 200-300 300 | $\Delta H (298) = -52 \text{ kJ/mol}$ $2.5 \times 10^{-12} \exp(-(600 \pm 300)/T)$ 3.4×10^{-13} (a) Based on room temp. value of Bemand, Clyne, Watson; temp dependence estimated | 1-5 |

Unchanged from NASA 1010. Arrhenius expression was estimated based on 298 K data reported by Bemand, Clyne and Watson (1973)

REFERENCES

Bemand, P., Clyne, M. A., and Watson, R. T., "Reactions of Chlorine Oxide Radical. Part 4.-Rate Constants for the Reaction $\text{Cl} + \text{OClO}$, $\text{O} + \text{OClO}$, $\text{H} + \text{OClO}$, $\text{NO} + \text{OClO}$ and $\text{O} + \text{ClO}$," *J. Chem. Soc., Faraday Trans. I* **69**, 1356-1374 (1973)

NASA RP-1010, "Chlorofluoromethanes and the Stratosphere"
 E. D. Hudson, Editor, August 1977 This reference contains the NASA (1977) rate constant recommendations.
 NASA (1979), Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future,"
 E. D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the June 1979 Harpers Ferry Workshop).

E. P. Hampson
 June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Uncert Factor
at 298K, notes

| No | Reaction/Reference | Temp- Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncert Factor at 298K, notes |
|-------|--|------------------|---|---------------------------------|
| 9,408 | NO + CH ₃ (·M) → CH ₃ NO (·M) Laufer, Bass (1975) | 298 | $10^{11} \frac{k}{s}$ c3 0.45 100 700 | (a) |
| | Basso, et al (1970) van den Bergh, Callear (1971) | 298 295 | 4 x 10 ⁻¹² 1.7 x 10 ⁻¹¹ (a) Values are based on k(CH ₃ + CH ₃) = 9.5 x 10 ⁻¹¹ given in Bass, Laufer (1973). (b) 2nd order high pressure limit | (b) (b) |

No recommendation

REFERENCES

- Basso, N., James, D. G. L., and Suert, R. D., "A Quantitative Study of Alkyl Radical Reactions by Kinetic Spectroscopy, Part I, Mutual Combination of Methyl Radicals and Combination of Methyl Radicals with Nitric Oxide," Int. J. Chem. Kinet. 2, 215-234 (1970)
- Laufer, A. E., and Bass, A. M., "Rate Constants of the Combination of Methyl Radicals with Nitric Oxide and Oxygen," Int. J. Chem. Kinet. 7, 639-648 (1975)
- van den Bergh, N. E., and Callear, A. E., "Spectroscopic Measurement of the Rate of the Gas-Phase Combination of Methyl Radicals with Nitric Oxide and Oxygen at 295 K," Trans. Faraday Soc. 67, 2017-2024 (1971)

R. F. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Temp. Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncertainty Factor at 298K, notes |
|------|--|------------------|---|--------------------------------------|
| | | | | |
| 9.51 | NO + CH ₃ O ₂ → CH ₃ O + NO ₂ (a) → CH ₂ O + HONO (b) → CH ₃ O ₂ NO (c) | | ΔH (298) = - 50 kJ/mol ΔH (298) = -286 kJ/mol | |
| | NASA (1979) eval | 200-300 | k _a = 7 × 10 ⁻¹² exp((0±500)/T) | 3 |
| | CODATA (1979) eval | 298 | k _a = 7.05 × 10 ⁻¹² | 2 |
| | Plumb, et al (1979) | 295 | k _a = (9±2) × 10 ⁻¹² | |
| | Cox, Tyndall (1979) | 292 | k _a = (6.5±2) × 10 ⁻¹² | |
| | Cox, et al (1976a) | 292 | k _a ≈ 1.2 × 10 ⁻¹² | lower limit (a) |
| | Pate, Finlayson, Pitts (1974) | 296 | (a) based on value of k(CH ₃ O ₂ + CH ₃ O ₂) | |
| | Simonaitis, Weicklen (1974) | 298 | Reaction proceeds exclusively through channel (a) k _a /k = 0.80 ± 0.15 (k = k _a + k _b + k _c) | |

The value for k(298) is the average of those reported by Plumb et al (1979), and by Cox and Tyndall (1979). Preliminary data of Sander and Watson (1979) supports the recommendation

REFERENCES

- CODATA(1979). Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.
- Cox, R. A., Derwent, R. G., Holt, P. M., and Kerr, J. A., "Photo-oxidation of Methane in the Presence of NO and NO₂," J. Chem. Soc. Faraday Trans. 1 72, 2044-2060 (1976a)
- Cox, R. A., and Tyndall, G., Chem. Phys. Lett. (submitted for publication, 1975)
- NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," P. D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the June 1979 Harpers Ferry Workshop).
- Pate, C. T., Finlayson, B. J., and Pitts, J. N., Jr., "A Long Path Infrared Spectroscopic Study of the Reaction of Methylperoxy Free Radicals with Nitric Oxide," J. Am. Chem. Soc. 96, 6554-6558 (1974)

Plumb, L. C., Ryan, K. R., Steven, J. R., and Mulcahy, M. F. R.,
"Kinetics of the reaction of CH_3O_2 with NO ," *Chem. Phys. Lett.* **63**,
255-258 (1979)

Sander, S., and Watson, R. T., private communication, 1979.
Simonsaitis, V., and Weicklen, J., "Reactions of CH_3O_2 with NO and NO_2 ,"
J. Phys. Chem. **78**, 2417-2421 (1974)

R. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No | Reaction/Reference | Temp. Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncert. Factor at 298K, notes |
|--------|---|------------------|---|--|
| 10,104 | $\text{NO}_2 + \text{NO}_2 \rightarrow \text{M} + \text{N}_2\text{O}_4 + \text{M} \quad (1)$ $\text{N}_2\text{O}_4 \rightarrow \text{M} + \text{NO}_2 + \text{NO}_2 + \text{M} \quad (2)$ Baulch, et al (1973) review | 250-350 | $k_f = 3.0 \times 10^{-35} \exp(1040/T) \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$ (a) corrected expression; $k_f = k_{f,\text{eq}}$ $k_r = 4.2 \times 10^{-7} \exp(-5550/T)$ $k_r = 3.3 \times 10^{-7} \exp(-5540/T)$ | $\text{M} = \text{N}_2$ $\text{M} = \text{N}_2$ $\text{M} = \text{N}_2$ $\text{M} = \text{N}_2$ 1.3 (a) 1.3 |
| | Schofield (1973) review | 250-350 | | |

$\Delta H (298) = -57 \text{ kJ/mol}$

This evaluation accepts the recommendations in the review of Baulch et al (1973)

REFERENCES

- Baulch, D. L., Drysdale, D. D., and Horne, D. G., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 2: Homogeneous Gas Phase Reactions of the H_2 - N_2 - O_2 System," (Butterworths, London, 1973)
- Schofield, K., "Evaluated Chemical Kinetic Rate Constants for Various Gas Phase Reactions," J. Phys. Chem. Ref. Data **2**, 25-84 (1973)
- B. P. Hampson
 May 1978

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No | Reaction/Reference | Temp. Range/K | Reaction Rate Constant $k/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$ | Uncert. Factor at 298K, notes |
|--------------------|--|---------------|---|----------------------------------|
| 1 ⁰ .11 | $\text{NO}_2 + \text{NO}_3 \rightarrow \text{NO}_2 + \text{O}_2 + \text{NO} \text{ (r)}$ | | $\Delta H (298) = 19 \text{ kJ/mol}$ | |
| 4.9.1 ^a | $\text{O}_2 + \text{NO} + \text{NO}_2 \rightarrow \text{NO}_2 + \text{NO}_3 \text{ (r)}$ | | | |
| | *Baulch, et al (1973) review | 300-850 | $k_1 = 2.3 \times 10^{-13} \exp(-1000/T)$ | 2-5 (a) |
| | | 300-500 | $k_2 = k_1/E_{\text{eq}} = 8 \times 10^{-14} \exp(400/T) \text{cm}^6\text{molecule}^{-2}\text{s}^{-1}$ | 2.5 |
| | Graham, Johnston (1978) | 338-396 | $k_2 = 2.5 \times 10^{-14} \exp(-1230/T)$ | |
| | | | (a) Based on $\text{N}_2\text{O}_5 + \text{M} \rightarrow \text{NO}_2 + \text{NO}_3 + \text{M}$ and $2\text{NO}_2 \rightarrow 2\text{NO} + \text{O}_2$ | |

This evaluation accepts the recommendations in the review of Baulch et al (1973)

REFERENCES

- Baulch, D. L., Drysdale, D. D., and Horne, D. G., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 2: Homogeneous Gas Phase Reactions of the H_2 - N_2 - O_2 System," (Butterworths, London, 1973)
- Graham, R. A., and Johnston, R. S., "The Photochemistry of NO_3 and the Kinetics of the N_2O_5 - O_3 System," J. Phys. Chem. **82**, 254-268 (1978)

R. F. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No | Reaction/Reference | Tempo Range/K | Reaction Rate Constant k/cm ⁶ molecule ⁻² s ⁻¹ | Uncert Factor at 298K, notes |
|------------------|--|---------------|---|---------------------------------|
| 10, 11M 14, M | NO ₂ + NO ₃ + M → N ₂ O ₅ + M (f) N ₂ O ₅ + M → NO ₂ + NO ₃ + M (r) NASA (1979) eval | 200-300 | ΔH (298) = - 93 kJ/mol k _f = (1.4±0.7) x 10 ⁻³⁰ (T/300) ^{-2.8±1.0} , M = N ₂ k _r = (9.0±4.5) x 10 ⁻¹³ (T/300) ^{0.7} cm ³ molecule ⁻¹ s ⁻¹ | |
| | CODATA (1979) eval | 300-340 | k _f = 1.5 x 10 ⁻³⁰ (T/300) ^{-4.6} , M = N ₂ | 2 |
| | | 200-400 | k _f = 5 x 10 ⁻¹² cm ³ molecule ⁻¹ s ⁻¹ | 2 |
| | | 300-340 | k _r = 8.8 x 10 ⁻⁶ exp(-9700/T) cm ³ molecule ⁻¹ s ⁻¹ | 2 |
| | | 273-300 | k _r = 5.7 x 10 ⁻¹⁴ exp(-10600/T) s ⁻¹ | 2 |
| | Baulch, et al (1973) review | 300 | k _f = 2.8 x 10 ⁻³⁰ | 2 (a) |
| | | 300 | k _f = 3.8 x 10 ⁻¹² cm ³ molecule ⁻¹ s ⁻¹ | 2.5 (a) |
| | | 300-340 | k _r = 2.2 x 10 ⁻⁵ exp(-9700/T) cm ³ molecule ⁻¹ s ⁻¹ | 2 (a) |
| | | 273-300 | k _r = 5.7 x 10 ⁻¹⁴ exp(-10600/T) s ⁻¹ | 2.5 (a) |
| | Graham, Johnston (1978) | 298-329 | K _{eq} = 1.2 x 10 ⁻²⁷ exp(+11180/T)cm ³ molecule ⁻¹ | (b) |
| | | 273-300 | k _f = 1.48 x 10 ⁻¹³ exp(+861/T)cm ³ molecule ⁻¹ s ⁻¹ | (c) |
| | | | k _r = 1.24 x 10 ⁻¹⁴ exp(-10317/T)s ⁻¹ | |
| | Connell, Johnston (1979) | 262-307 | k _r = 6.1 x 10 ⁻⁶ exp(-9570/T) cm ³ molecule ⁻¹ s ⁻¹ | |
| | | | k _r = 1.78 x 10 ⁻¹⁷ exp(-12540/T)s ⁻¹ | |
| | | | (a) k _f = K _{eq} k _r , M = N ₂ O ₅ + NO | |
| | | | (b) 2d order rate const at 1 atm | |
| | | | (c) 1st order rate const at 1 atm | |

Recommendation is based on results reported by Connell and Johnston (1979) and private communication from Dr. Albritton, F. Fehsenfeld and A. Viggiano (1979)

REFERENCES

- Baulch, D. L., Drysdale, D. D., and Horne, D. G., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 2: Homogeneous Gas Phase Reactions of the H₂-N₂-O₂ System," (Butterworths, London, 1973)
- CODATA(1979): Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.
- Connell, P., and Johnston, R. S., "The Thermal Dissociation of N₂O₅ in N₂," Geophys. Res. Lett. **5**, 553-556 (1979)

Graham, R. A., and Johnston, R. S., "The Photochemistry of NO_3 and the Kinetics of the N_2O_5 System," J. Phys. Chem. **82**, 254-268 (1978) NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA EP 1049 "The Stratosphere: Present and Future,"

R. D. Hudson and R. L. Reed, Editors, Dec. 1979 (report of the June 1979 Harpers Ferry Workshop).

F. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No | Reaction/Reference | Temp. Range/K | Reaction Rate Constant $k/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$ | Uncert. Factor at 298K, notes |
|--------|---|------------------|--|----------------------------------|
| 1C, 16 | $\text{NO}_2 + \text{NH}_2 \rightarrow \text{products}$ Jayanty, et al (1975d) | 300 | $k = k(\text{NO} + \text{NH}_2)$ | |

No recommendation

REFERENCES

Jayanty, P. K. M., Simonaitis, R., and Reichlen, J., "The Reaction of NH_2 with NO_2 ." (Department of Chemistry and Ionosphere Research Laboratory, Penn. State Univ., Pa. 16802, 1975d)

R. F. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No | Reaction/Reference | Temp. Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncert. Factor at 298K, notes |
|--------------------|--|------------------|--|----------------------------------|
| 1 ^c .17 | NO ₂ + NH ₃ → NH ₂ + HNO ₂ Bedford, Thomas (1972) | 615-660 | ΔH (298) = 118 kJ/mol 6.7 x 10 ⁻¹² exp(-13900/T) | |

No recommendation

REFERENCES

Bedford, G., and Thomas, J. H., "Reaction between Ammonia and Nitrogen Dioxide," J. Chem. Soc., Faraday Trans. 1 68, 2163-2170 (1972)

R. F. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No | Reaction/Reference | Temp. Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncert. Factor at 298K, notes |
|---------------------|---|------------------|--|----------------------------------|
| 1 ^c , 18 | $\text{NO}_2 + \text{H} \rightarrow \text{NO} + \text{H}_2$ (1) | | $\Delta H(298) = -122 \text{ kJ/mol}$ | |
| 9, 19 | $\text{NO} + \text{H} \rightarrow \text{NO}_2 + \text{H}$ (r) | | | |
| | This survey | | | |
| | Wagner, et al (1976a) | 250-500 | $k_1 = 5.8 \times 10^{-10} \exp(-450/T)$ | 1.3 |
| | Clyne, Monkhouse (1977) | 243-461 | $k_2 = 7.1 \times 10^{-10} \exp(-505 \pm 84/T)$ | |
| | Bemand, Clyne (1977) | 268-653 | $k_3 = 4.80 \times 10^{-10} \exp(-400 \pm 70/T)$ | |
| | Baulch, et al (1973) review | 298 | $k_4 = 1.13 \pm 0.22 \times 10^{-10}$ | |
| | | 298-633 | $k_5 = 5 \times 10^{-12} \exp(-15100/T)$ (a) $k_5 = k_4/K_{eq}$ | 2 (a) |

Recommended expression is based on the results reported in the two temperature dependent studies

REFERENCES

- Baulch, D. L., Drysdale, D. D., and Horne, D. G., "Evaluated Kinetic Data for High Temperature Reactions, Vol 2: Homogeneous Gas Phase Reactions of the H_2 - H_2 - O_2 System," (Butterworths, London, 1973)
- Bemand, P. P., and Clyne, M. A. A., "Atomic Resonance Fluorescence for Rate Constants of Rapid Bimolecular Reactions, Part 6.-Hydrogen Atom Reactions: $\text{H} + \text{Cl}_2$ from 300 to 730K and $\text{H} + \text{NO}_2$ at 298K," J. Chem. Soc., Faraday Trans. II 73, 394-405 (1977)
- Clyne, M. A. A., and Monkhouse, P. B., "Atomic Resonance Fluorescence for Rate Constants of Rapid Bimolecular Reactions, Part 5.-Hydrogen Atom Reactions: $\text{H} + \text{NO}_2$ and $\text{H} + \text{O}_3$," J. Chem. Soc., Faraday Trans. II 73, 298-309 (1977)
- Wagner, G. G., Welzbacher, U., and Zellner, R., "Rate Measurements for the Reactions $\text{H} + \text{NO}_2 \rightarrow \text{OH} + \text{NO}$ and $\text{H} + \text{NOCl} \rightarrow \text{HCl} + \text{NO}$ by Lyman- α Fluorescence," Ber. Bunsenges. Phys. Chem. 80, 1023-1027 (1976)

R. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Reaction/Reference
Temp.
Range/K

Reaction Rate Constant
k/cm⁶molecule⁻²s⁻¹

Uncert. Factor
at 298K, notes

| | | | | |
|---------|---|----------|--|-----|
| 1C, 19M | NO ₂ + NO + M → HNO ₃ + M (r) | 200-300 | k _f = (2.6 ± 0.3) × 10 ⁻³⁰ (T/300) ^{-2.9 ± 0.7} , M = N ₂ | |
| 26, M | HNO ₃ + M → NO + NO ₂ + M (r) | | k _{f,0} = (2.4 ± 1.2) × 10 ⁻¹¹ (T/300) ^{-1.3 ± 1} cm ³ molecule ⁻¹ s ⁻¹ | |
| | NASA (1979) eval | | k _f = 2.6 × 10 ⁻³⁰ (T/300) ^{-2.7} , M = N ₂ | 1.3 |
| | CODATA (1979) eval | 220-360 | k _{f,0} = 1.6 × 10 ⁻¹¹ cm ³ molecule ⁻¹ s ⁻¹ | 1.6 |
| | Anastasi, Smith (1976) | 296 | k _f = 2.6 × 10 ⁻³⁰ M = N ₂ | |
| | | | Rel. Efficiencies: N ₂ (1.0), He(0.34), Ar(0.42), O ₂ (0.68), SF ₆ (2.5) | |
| | | 220-550 | n = -2.6 for temp dependence of form T ⁿ , M = N ₂ | |
| | | | values given for bimolecular rate constant over ranges T = 220-550K and [N ₂] = 3 × 10 ¹⁷ to 1.6 × 10 ¹⁹ molecule cm ⁻³ | |
| | Baulch, et al (1973) review | 273-400 | k _f = 3.6 × 10 ⁻³² exp(•1100/T) | 1.6 |
| | | | M = He | |
| | | 800-1200 | k _f = 2.7 × 10 ⁻⁹ exp(-15400/T) cm ³ molecule ⁻¹ s ⁻¹ | 2.5 |
| | | | M = Ar | |
| | Anderson, et al (1974) | 300 | k _{f,0} = 8 × 10 ⁻¹² cm ³ molecule ⁻¹ s ⁻¹ | 2.5 |
| | | 295-450 | k _f = 2.3 ± 0.5 × 10 ⁻³⁰ × (295/T) ^{2.5} | |
| | | | M = N ₂ | |
| | | | Relative efficiencies: N ₂ (1.0), Ar(0.42), He(0.43) | |
| | Howard, Evenson (1974) | 256 | k _f = 2.9 ± 0.4 × 10 ⁻³⁰ M = N ₂ | |
| | Gordon, Mulac (1975) | 435 | k _f = 5.3 × 10 ⁻¹² cm ³ molecule ⁻¹ s ⁻¹ | |
| | | | (2nd order rate constant at 1 atm H ₂ O vapor) | |
| | Harris, Wayne (1975) | 300 | 15 ± 5 × 10 ⁻³¹ M = Ar | |
| | | | 26 ± 10 × 10 ⁻³¹ , M = N ₂ | |
| | Atkinson, Perry, Pitts (1976) | 258 | k _f = (1.0 ± 0.1) × 10 ⁻³⁰ M = Ar | |
| | | | Values given for bimolecular rate constant over pressure range 25-646 torr Ar | |

REFERENCES

- Anastasi, C., and Smith, I. W. M., "Rate Measurements of Reactions of OH by Resonance Absorption Part 5: Rate Constants for OH + NO₂ (+ M) → HNO₃ (+ M) Over a Wide Range of Temperature and Pressure," J. Chem. Soc., Faraday Trans. II 72, 1459-1468 (1976)
- Anderson, J. O., Margitan, J. O., and Kaufman, F., "Gas Phase Recombination of OH with NO and NO₂," J. Chem. Phys. 60, 3310-3317 (1974)

- Atkinson, R., Perry, R. A., and Pitts, J. N., Jr., "Rate Constants for the Reactions of the OH Radical with NO_2 (N - Ar and N_2) and SO_2 (N - Ar)," J. Chem. Phys. **65**, 306-310 (1976)
- Baulch, D. L., Drysdale, D. B., and Horne, D. G., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 2: Homogeneous Gas Phase Reactions of the H_2 - H_2 -O System," (Butterworths, London, 1973)
- CODATA(1979): Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.
- Gordon, S., and Mulaic, V. A., "Reaction of the CH_2X_2 Radical Produced by the Pulse Radiolysis of Water Vapor," Int. J. Chem. Kinet., Symp. No. 1, 289-299 (1975)
- Harris, G. E., and Wayne, R. P., "Reaction of Hydroxyl Radicals with NO , NO_2 and SO_2 ," J. Chem. Soc., Faraday Trans. 1 **71**, 610-617 (1975)
- Revard, G. J., and Evenson, K. E., "Laser Magnetic Resonance Study of the Gas Phase Reactions of OH with CO, NO , and NO_2 ," J. Chem. Phys. **61**, 1943-1952 (1974)
- NASA (1979), Recommendations of the NASA Panel for Late Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," E. D. Eubank and E. L. Reed, Editors, Deco 1979 (report of the June 1979 Barbers Ferry Workshop).
- E. P. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No | Reaction/Reference | Temp. Range/K | Reaction Rate Constant k/cm ³ molecule ⁻² s ⁻¹ | Uncert Factor at 298K, notes |
|--------|---|-------------------|--|---------------------------------|
| 10.20W | NO ₂ + NO ₂ + M → NO ₂ NO ₂ + M NASA (1979) eval | 200-300 | $k = (2.1 \pm 0.4) \times 10^{-31} (T/300)^{-5.2}$, M = N ₂ $k_{\infty} = (6.5 \pm 3.3) \times 10^{-12} (T/300)^{-5.2}$ cm ³ molecule ⁻¹ s ⁻¹ | |
| | CODATA (1979) eval Howard (1977) | 300 300 | $k = 2.1 \times 10^{-31}$ $(2.09 \pm 0.52) \times 10^{-31}$ M = N ₂ Rel. eff: N ₂ (1.0), He(0.48); O ₂ (0.72); NO ₂ (3.2) $k(\text{NO}_2 + \text{NO}_2 \rightarrow \text{HONO} + \text{O}_2) < 3 \times 10^{-15}$ | |
| | Cox, Patrick (1979) Simonaitis, Heicklen (1977) | 283 285 295 | $k = (2.5 \pm 0.5) \times 10^{-31}$ $k(\text{M})/k(\text{NO}_2 + \text{NO}) = 0.61$ $k(\text{M})/k(\text{NO}_2 + \text{NO}) = 0.036$ (a) M = 700 torr H ₂ . Rxn to give HONO + O ₂ is negligible | (a) (a) |

REFERENCES

- CODATA(1979). Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.
- Cox, R. A., and Patrick, E. "Kinetics at the Reaction of NO₂ + NO₂(+M) → NO₂NO₂ using Molecular Modulation Spectrometry, Int. J. Chem. Kinet., **11**, 635-648 (1979)
- Howard, C. J. "Kinetics of the Reaction of NO₂ with NO₂," J. Chem. Phys. **62**, 5258-5263 (1977)
- NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA SP 1049 "The Stratosphere: Present and Future," R. D. Hudson and E. L. Reed, Editors, Dec. 1979 (report of the June 1979 Harpers Ferry Workshop).
- Simonaitis, E., and Heicklen, J. "The Temperature Dependence of the Reactions of NO₂ with NO and NO₂," Int. J. Chem. Kinet. **10**, 67-87 (1978)
- R. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No | Reaction/Reference | Temp. Range/K | Reaction Rate Constant $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | Uncert Factor at 298K, notes |
|-------|---|------------------|--|---------------------------------|
| 1f.28 | $\text{NO}_2 + \text{SO}_2 \rightarrow \text{SO}_3 + \text{NO}$ Davis (1976) | 300 | $\Delta H (298) = -42 \text{ kJ/mol}$ $k < 2 \times 10^{-24}$ | preliminary |

No recommendation

REFERENCES

Davis, D. D., "Absolute Rate Constants for Elementary Reactions of Atmospheric Importance: Results from the University of Maryland Gas Kinetics Laboratory," Report 3 (Univ. of Maryland, College Park, Md. 20742, 1976)

D. F. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Uncert Factor
at 298K, notes

| No | Reaction/Reference | Temp. Range/K | Reaction Rate Constant k/cm ⁶ molecule ⁻² s ⁻¹ | Uncert Factor at 298K, notes |
|---------|---|------------------|---|---------------------------------|
| 1C, 35M | NO ₂ + Cl + M - products NASA (1979) eval | 200-300 | $k = (1.6 \pm 1.0) \times 10^{-30} (T/300)^{-1.9 \pm 1}$ $k_{\infty} = (3.0 \pm 1.5) \times 10^{-11} (T/300)^{-1 \pm 1} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | |

Reaction proceeds through two reaction channels to give both ClONO and ClNO₂ as products;
see Niki et al (1978) and Chang et al (1979)

REFERENCES

- Chang, J. S., Baldwin, A. Co., and Golden, D. M., "An Explanation of the Preferential Formation of Less Stable Isomers in Three-Body Reactions: Cl + NO₂ + M; Cl + NO₂ + M," J. Chem. Phys. **71**, 2021-2024 (1979)
- NASA (1979), Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," E. D. Hudson and E. L. Reed, Editors, Dec. 1979 (report of the June 1975 Harpers Ferry Workshop).
- Niki, S., Baker, P. D., Savage, G. M., and Breitenbach, L. P., "Fourier Transform IR Spectroscopic Observation of Chlorine Nitrite, ClONO, Formed Via Cl + NO₂(+M) - ClONO(+M)," Chem. Phys. Lett. **59**, 78-79 (1978)
- R. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Temp. Range/K | Reaction Rate Constant $k/\text{cm}^3 \text{molecule}^{-2} \text{s}^{-1}$ | Uncert. Factor at 258K, notes |
|--------|---|------------------|---|----------------------------------|
| 10,38F | $\text{NO}_2 + \text{F} + \text{M} \rightarrow \text{FNO}_2 + \text{M}$ - FONG + M NASA (1975) eval | 200-300 | $k = (1.340.7) \times 10^{-30} (T/300)^{-1.7}$, $M = \text{N}_2$ $k_{\infty} = (341.5) \times 10^{-11} (T/300)^{-1.61} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | |

Estimated values; no data

REFERENCES

NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future,"
B. D. Hudson and E. L. Reed, Editors, Dec. 1975 (report of the
June 1975 Harpers Ferry Workshop).

B. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Temp. Range/K | Reaction Rate Constant k/cm ³ molecule ⁻² s ⁻¹ | Uncert. Factor at 298K, notes |
|--------|--|--------------------------------------|---|----------------------------------|
| 15,36M | NO ₂ + ClO + M → ClONO ₂ + M | | ΔH (298) = -105 kJ/mol | |
| | NASA (1979) eval | 200-300 | k = (1.6±0.2) × 10 ⁻³¹ (T/300) ^{-3.4±0.3} , M = N ₂ k = (3.5±1.7) × 10 ⁻³² (T/300) ^{-3.8±1} , M = N ₂ k _∞ = (1.5±0.7) × 10 ⁻¹¹ (T/300) ^{-1.9±1} cm ² molecule ⁻¹ s ⁻¹ | |
| | CODATA (1979) eval | 250-400 | k = 1.07 × 10 ⁻³¹ (T/300) ^{-3.0} , M = N ₂ k _∞ = 1.2 × 10 ⁻¹¹ cm ² molecule ⁻¹ s ⁻¹ | 1.3 2.5 |
| | Birks, et al (1977) | 250-356 | (4.40 ± 0.66) × 10 ⁻³³ exp(1087/T) M = N ₂ 9.97 ± 0.28 × 10 ⁻³² M = He | |
| | Leu, Lin, DeMore (1977) | 297 298-417 | (3.69 ± 0.24) × 10 ⁻³³ exp(1150/T) M = N ₂ (2.66 ± 0.35) × 10 ⁻³³ exp(1140/T) M = He | |
| | Zahniser, Chang, Kaufman (1977) | 248-417 251-365 251-365 257 | (3.54 ± 0.06) × 10 ⁻³³ exp(950/T) M = He 5.53 × 10 ⁻²⁴ T ^{-3.15} M = He 1.52 × 10 ⁻³¹ M = N ₂ | |

NASA (1979) gives two distinct recommendations for k. The first corresponds to the measured rate constant for disappearance of the reactants. The second has been calculated from the rate of decomposition of ClONO₂ (Knuth, 1978) and the equilibrium constant. The discrepancy may be due to the production of isomers through different reaction channels. See the discussion in Chang et al (1979)

REFERENCES

- Birks, J. W., Shoemaker, B., Leck, T. J., Borders, B. A., and Hart, L. J.,
 "Studies of Reactions of Importance in the Stratosphere. II: Reactions
 Involving Chlorine Nitrate and Chlorine Dioxide," J. Chem. Phys. **64**,
 4591-4595 (1977)
- Chang, J. S., Baldwin, A. C., and Golden, D. M., "An Explanation of the
 Preferential Formation of Less Stable Isomers in Three-Body Reactions:
 Cl + NO₂ + M; ClO + NO₂ + M," J. Chem. Phys. **71**, 2021-2024 (1979)
- CODATA(1979): Recommendations of the CODATA Task Group on Chemical
 Kinetics. To be published in the Journal of Physical and Chemical
 Reference Data.
- Knuth, H.-D., "Über den thermischen Zerfall von ClONO₂ in
 Gegenwart von NO, ClNO und N₂," Ber. Bunsenges. Phys.
 Chem. **82**, 212-216 (1978)

Iou, M. T., Lin, C. L., and DeMore, W. B., "Rate Constant for Formation of Chlorine Nitrate by the Reaction $\text{ClO} + \text{NO}_2 + \text{M}$," J. Phys. Chem. **81**, 190-195 (1977)

NASA (1979). Recommendations of the NASA Panel for Data Evaluation. Published in NASA RP 1049 "The Stratosphere: Present and Future," B. D. Hudson and E. L. Reed, Editors, Dec. 1979 (report of the June 1979 Harpers Ferry Workshop).

Zahniser, M. S., Chang, J. S., and Kaufman, F., "Chlorine Nitrate: Kinetics of Formation by $\text{ClO} + \text{NO}_2 + \text{M}$ and of Reaction with OH ," J. Chem. Phys. **67**, 597-1003 (1977)

B. F. Neapson
June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Temp. Range/K | Reaction Rate Constant $k/cm^6 molecule^{-2} s^{-1}$ | Uncert. Factor at 258K, notes |
|---------|--|------------------|---|----------------------------------|
| 10.3cBr | $NO_2 + BrO \rightarrow N + BrONO_2 + M$ | | $\Delta H(298) = -138 \text{ kJ/mol}$ | |
| | NASA (1979) eval | 200-300 | $k = 3.2 \times 10^{-31} (T/300)^{-3.4}, M = N_2$ | |
| | CODATA (1979) eval | 200-400 | $k = 3 \times 10^{-31} (T/300)^{-3}, M = N_2$ | 2x5 |
| | | | $k_a = 1.2 \times 10^{-11} \text{ cm}^3 molecule^{-1} s^{-1}$ | |
| | Watson, Sander (1978) | 258 | $k = 3 \times 10^{-31}, M = N_2$ | provisional data |

Estimated value; taken as twice the value for $NO_2 + ClO \rightarrow M$

REFERENCES

CODATA(1979). Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.

NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," E. D. Hudson and E. L. Reed, Editors, Dec. 1975 (report of the June 1975 Harpers Ferry Workshop).

Watson, R. L., and Sander, S. P., 1978, Manuscript in preparation.

R. E. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| Ref | Reaction/Reference | Temp. Range/K | Reaction Rate Constant $k/\text{cm}^6\text{molecule}^{-2}\text{s}^{-1}$ | Uncertainty Factor at 258K, notes |
|--------|--|------------------|---|--------------------------------------|
| 10,32F | $\text{NO}_2 + \text{FG} + \text{M} \rightarrow \text{FONO}_2$ | | $\Delta H (298) = -132 \text{ kJ/mol}$ | |
| | NASA (1979) eval | 200-300 | $k = (8.366,0) \times 10^{-31} (T/300)^{-0.7}, \text{M} = \text{N}_2$ | |
| | | | $k_{\infty} = (2.081,0) \times 10^{-11} (T/300)^{-1.051,5} \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1}$ | |
| | CODATA (1975) eval | 200-400 | $k = 1.7 \times 10^{-31} (T/300)^{-3}, \text{M} = \text{N}_2$ | 5 |
| | | | $k_{\infty} = 1.2 \times 10^{-11} \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1}$ | 5 |

Estimated values; no data

REFERENCES

CODATA(1979). Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.

NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA EP 1049 "The Stratosphere: Present and Future," E. De Hudson and E. I. Reed, Editors, Dec. 1979 (report of the June 1975 Harpers Ferry Workshop).

E. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No | Reaction/Reference | Temp. Range/K | Reaction Rate Constant $k/\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ | Uncert. Factor at 298K, notes |
|---------------------|--|------------------|---|----------------------------------|
| 1 ^c .45 | $\text{NO}_2 + \text{CH}_3 \rightarrow \text{CH}_3\text{O} + \text{NO}$ Glanzer, Troe (1974) | 300-1400 | 3.3×10^{-11} (a) Based on $k/k(\text{CH}_3 + \text{NO}) = 3-3$ at room temperature and on shock wave pyrolysis of CH_3NO_2 | 2 (a) |
| 1 ^c .49W | $\text{NO}_2 + \text{CH}_3 (\cdot \text{M}) \rightarrow \text{CH}_3\text{NO}_2 (\cdot \text{M})$ Glanzer, Troe (1974) | 295 | $2.8 \times 10^{-11} \text{ cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ (a) Based on high pressure limit rate ratio $k/k(\text{CH}_3 + \text{NO}) = 1.07$ | 2 (a) |
| 1 ^c .49M | $\text{NO}_2 + \text{CH}_3 + \text{M} \rightarrow \text{CH}_3\text{NO}_2 + \text{M}$ Glanzer, Troe (1974) | 900-1400 | $6.9 \times 10^{-31} (T/1000)^{-6} \text{ cm}^6 \text{molecule}^{-2} \text{s}^{-1}$, $\text{M} = \text{Ar}$ (a) $k_f = k_r K_{\text{eq}}$ | (a) |

No recommendations

REFERENCES

Glanzer, K., and Troe, J., "Reactions of Alkyl Radicals in the Shock Wave-Induced Pyrolysis of Nitroalkanes," Ber. Bunsenges. Phys. Chem. **78**, 182-184 (1974)

R. P. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No | Reaction/Reference | Temp- Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncert- Factor at 298K, notes |
|-------|--|------------------|--|----------------------------------|
| 1C.51 | $\text{NO}_2 + \text{CH}_3\text{O}_2 \rightarrow \text{CH}_3\text{O}_2\text{NO}_2$ (a) $\rightarrow \text{CH}_3\text{O} + \text{HONO}_2$ (b) $\rightarrow \text{CH}_3\text{O} + \text{NO}_3$ (c) Reichlen (1973) review | 298 | ΔH (298) = - 80 kJ/mol = -284 kJ/mol = 45 kJ/mol $k_a/k_c = 0.75 \pm 0.05$ $k_b/k_c = 0.25 \pm 0.1$ $k_c/k_c < 0.1$ | |

No recommendation

REFERENCES

Reichlen, J., "Photochemical and Rate Data for Methyl Nitrite, Methoxy and Methylperoxy," Chemical Kinetics Data Survey V, Sixty-six Contributed Rate and Photochemical Data Evaluations on Ninety-four Reactions, NBSIR 73-206, D. Garvin, Ed., National Bureau of Standards, Washington, D.C (1973) pages 43-48

R. F. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Temp. Range/K | Reaction Rate Constant $k/cm^3 \text{ molecule}^{-2} s^{-1}$ | Uncert. Factor at 258K, notes |
|--------|--|------------------|--|----------------------------------|
| 10,51M | $NO_2 + CH_3O_2 \rightarrow M + CH_3O_2NO_2 + M$ NASA (1979) eval | 200-300 | $\Delta H (298) = -60 \text{ kJ/mol}$ $k = (2.0 \pm 1.0) \times 10^{-30} (T/300)^{-4 \pm 2}, M = N_2$ $k_{\infty} = (0.5 \pm 3.0) \times 10^{-12} (T/300)^{-4 \pm 2}$ | |
| | CODATA (1979) eval Cox, Tyndall (1979) | 200-300 276 | $1.6 \times 10^{-12} (1 \text{ atm air})$ $1.6 \times 10^{-12} (540 \text{ torr } N_2)$ $1.2 \times 10^{-12} (50 \text{ torr Ar})$ (a) Effective bimolecular rate constant in units of $cm^3 \text{ molecule}^{-1} s^{-1}$ | 3 (a) (a) (a) |

REFERENCES

- CODATA (1979). Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.
- Cox, J. A., and Tyndall, G. S., "Rate Constants for Reactions of CH_3O_2 in the Gas Phase," Chem. Phys. Lett. **65**, 357-360 (1979)
- NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," E. D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the June 1979 Harpers Ferry Workshop).

E. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No | Reaction/Reference | Temp Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncert Factor at 298K, notes |
|-------|---|--------------------|---|---------------------------------|
| 11.11 | $\text{NO}_3 + \text{NO}_3 \rightarrow 2\text{NO}_2 + \text{O}_2$ Graham, Johnston (1978) Baulch, et al (1973) review | 298-329 293-309 | $\Delta H (298) = -76 \text{ kJ/mol}$ $8.5 \times 10^{-13} \exp(-2450/T)$ $5 \times 10^{-12} \exp(-3000/T)$ (a) $-d[\text{NO}_3]/dt = 2k[\text{NO}_3]^2$. Based on rate of NO_3 decomp. in presence of N_2O_5 | (a) |

No recommendation

REFERENCES

- Baulch, D. L., Drysdale, D. D., and Horne, D. G., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 2: Homogeneous Gas Phase Reactions of the H_2 - N_2 - O_2 System," (Butterworths, London, 1973)
- Graham, D. A., and Johnston, H. S., "The Photochemistry of NO_3 and the Kinetics of the N_2O_5 - O_3 System," J. Phys. Chem. 82, 254-268 (1978)

D. F. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No | Reaction/Reference | Temp Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncert Factor at 298K, notes |
|-------|---|-----------------|--|---------------------------------|
| 11,28 | NO ₃ + SO ₂ → NO ₂ + SO ₃ Daubendiek, Calvert (1975) Davis (1976) | 300 300 | ΔP (298) = -137 kJ/mol k < 7 x 10 ⁻²¹ k < 1 x 10 ⁻²¹ | preliminary |

Note that this is an upper limit only

REFERENCES

- Daubendiek, P. L., and Calvert, J. G., "A Study of the N₂O₅-SO₂-O₃ Reaction System," Environ. Lett. **2**, 103-116 (1975)
- Davis, D. D., "Absolute Rate Constants for Elementary Reactions of Atmospheric Importance: Results from the University of Maryland Gas Kinetics Laboratory," Report 3 (Univ of Maryland, College Park, Md. 20742, 1976)
- D. F. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No | Reaction/Reference | Temp Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncert Factor at 298K, notes |
|-------|---|-----------------|--|---------------------------------|
| 11.28 | N ₂ + SO ₂ → NO ₂ + SO ₃ Shaubendiek, Calvert (1975) Davis (1976) | 300 300 | ΔF (298) = -137 kJ/mol k < 7 × 10 ⁻²¹ k < 1 × 10 ⁻²¹ | preliminary |

Note that this is an upper limit only

REFERENCES

- Shaubendiek, P. L., and Calvert, J. G., "A Study of the N₂O-SO₂-SO₃ Reaction System," Environ. Lett. **2**, 103-116 (1975)
- Davis, D. D., "Absolute Rate Constants for Elementary Reactions of Atmospheric Importance: Results from the University of Maryland Gas Kinetics Laboratory," Report 3 (Univ. of Maryland, College Park, Md. 20742, 1976)

D. F. Ransome
May 1978

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No | Reaction/Reference | Temp Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncert Factor at 298K, notes |
|-------|--|-----------------|--|---------------------------------|
| 13.18 | N ₂ O + N → N ₂ + NO (1) | | ΔH (298) = -261 kJ/mol | |
| 12.10 | N ₂ + NO → N ₂ O + N (r) | | | |
| | Albers, et al (1975) | 710-1111 | k _r = (3.6 ± 1.2) × 10 ⁻¹⁰ exp(-8710 + 350/T) | |
| | Baulch, et al (1973) review | 700-2500 | k _r = 1.3 × 10 ⁻¹⁰ exp(-7600/T) | 1.5 |
| | | | k _r = 5.4 × 10 ⁻¹² exp(-40400/T) | 1.5 (a) |
| | | | (a) k _r = k _r /K _{eq} corrected expression | |
| | Baldwin, et al (1973) | 773 | k _r = 4.3 × 10 ⁻¹⁵ | |

No recommendation

REFERENCES

- Albers, E. A., Moyermann, E., Schacke, R., Schatzko, K. J., Wagner, H. G., and Wolfrum, J., "Absolute Rate Coefficients for the Reaction of H-Atoms with N₂O and Some Reactions of CN Radicals," Symp. Combust. 15th (Combustion Institute, Pittsburgh, 1975) 765-773
- Baldwin, P. P., Gethin, A., and Walker, R. W., "Reaction of Hydrogen Atoms with Nitrous Oxide," J. Chem. Soc., Faraday Trans. I 69, 352-358 (1973)
- Baulch, D. L., Drysdale, D. D., and Horne, D. G., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 2: Homogeneous Gas Phase Reactions of the H₂-N₂-O₂ System," (Butterworths, London, 1973)

P. P. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Uncert Factor
at 258K, notes

Reaction/Reference Temp.
Range/K Reaction Rate Constant
k/cm³molecule⁻¹s⁻¹

No

upper limit only

| | | | |
|-------|---|-----|-------------------------------|
| 13.19 | N ₂ ⁺ + RH → products | | < 4 x 10 ⁻¹⁶ |
| | Chang, Kaufman (1977) | 480 | 3.8 ± 1-2 x 10 ⁻¹⁷ |
| | Bierman, et al (1976) | 298 | < 2 x 10 ⁻¹⁶ |
| | Atkinson, Perry, Pitts (1976a) | 258 | < 2 x 10 ⁻¹⁶ |
| | | 443 | < 2 x 10 ⁻¹⁴ |
| | Gordon, Mulac (1975) | 440 | |

This evaluation accepts the upper limit reported by Chang and Kaufman. It is consistent with the upper limits reported by Atkinson et al (1976a)

REFERENCES

- Atkinson, P., Perry, P. A., and Pitts, J. N., Jr., "Kinetics of the Reactions of OH Radicals with CH₄ and N₂O," Chem. Phys. Lett. **44**, 204-208 (1976a)
- Biermann, P. W., Zetzsch, C., and Stuhl, F., "Rate Constant for the Reaction of OH with N₂O at 298 K," Ber. Bunsenges. Phys. Chem. **80**, 905-911 (1976)
- Chang, J. A., and Kaufman, F., "Upper Limits of the Rate Constants for the Reactions of CFC₁₃(F-11), CF₂Cl₂(F-12), and N₂O with OH and Estimates of Corresponding Lower Limit of their Tropospheric Lifetimes," Geophys. Res. Lett. **4**, 192-194 (1977)
- Gordon, S., and Mulac, W. A., "Reaction of the OH(X²Π) Radical Produced by the Pulse Radiolysis of Water Vapor," Int. J. Chem. Kinet., Symp. No. 1, 289-299 (1975)

P. F. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Uncert Factor
at 298K, notes

Reaction/Reference Temp Reaction Rate Constant
Range/K $k/cm^3 molecule^{-1} s^{-1}$

No

13.36 $N_2O + ClO \rightarrow products$
NASA (1979) eval

200-300 $4.1 \times 10^{-12} \exp(-4260/T)$

Unchanged from NASA 1010. These upper limits are based on the data of Walker (reported in Clyne and Watson (1974a)). The upper limits shown for k (298) were actually determined from data collected at either 587 K or 670 K. The Arrhenius expressions were estimated based on this ~ 600 K data

REFERENCES

- Clyne, W. A. A., and Watson, W. T., "Kinetic Studies of Diatomic Free Radicals using Mass Spectrometry Part 2: Rapid Bimolecular Reactions Involving the ClO $X^2\pi$ Radical," J. Chem. Soc., Faraday Trans. 1 **70**, 2250-2259 (1974a)
- NASA 1010. "Chlorofluoromethanes and the Stratosphere" P. D. Hudson, Editor, August 1977 This reference contains the NASA (1977) rate constant recommendations.
- NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," W. D. Hudson and E. J. Peed, Editors, Dec. 1979 (report of the June 1979 Harpers Ferry Workshop).

v F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No | Reaction/Reference | Temp Range/K | Reaction Rate Constant $k/\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ | Uncert Factor at 293K, notes |
|-------|--|-----------------|--|---------------------------------|
| 13,45 | $\text{N}_2\text{O} + \text{CM} \rightarrow \text{products}$ Milks, Matula (1973) | 1169-1655 | $3.5 \times 10^{-13} \exp(-8650/T)$ | |

No recommendation

REFERENCES

Milks, D., and Matula, R. A., "A Single-Pulse Shock-Tube Study of the Reaction between Nitrous Oxide and Carbon Monoxide," Symp. Combust, 14th (Combustion Institute, Pittsburgh, 1973) 83-96

D. F. Hanson
May 1978

CHEMICAL KINETICS DATA SURVEY
 PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No | Reaction/Reference | Temp Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncert Factor at 298K, notes |
|-------|---|-----------------|--|---------------------------------|
| 14.22 | N ₂ O ₅ + H ₂ O → 2HNO ₃ Morris, Niki (1973) | 298 | ΔH (298) = - 40 kJ/mol 1.3 × 10 ⁻²⁰ | |

Note that this is an upper limit only. This result and earlier results are discussed in the review of Hanson et al (1973)

REFERENCES

- Hanson, R. P., (editor), "Survey of Photochemical and Rate Data for Twenty-Eight Reactions of Interest in Atmospheric Chemistry," J. Phys. Chem. Ref. Data 2, No. 2 pnc 267-312 (1973). These are revised versions of data sheets originally distributed as NBS Reports 10692 and 10828.
- Morris, E. D., Jr., and Niki, S., "Reaction of Dinitrogen Pentoxide with Water," J. Phys. Chem. 77, 1929-1932 (1973)
- R. P. Hanson
May 1978

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No | Reaction/Reference | Temp Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncert Factor at 298K, notes |
|-------|--|-----------------|--|---------------------------------|
| 14.28 | N ₂ O ₅ + SO ₂ → products Daubendiek, Calvert (1975) Davis (1976) | 300 300 | k < 4 x 10 ⁻²³ k < 8 x 10 ⁻²⁴ | preliminary |

Note that this is an upper limit only

REFERENCES

- Daubendiek, P. L., and Calvert, J. G., "A Study of the N₂O₅-SO₂-O₃ Reaction System," Environ. Lett. **2**, 103-116 (1975)
- Davis, D. D., "Absolute Rate Constants for Elementary Reactions of Atmospheric Importance: Results from the University of Maryland Gas Kinetics Laboratory," Report 3 (Univ. of Maryland, College Park, Md. 20742, 1976)

F. P. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| NO | Reaction/Reference | Temp Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncert Factor at 298K, notes |
|---------|--|-----------------|---|---------------------------------|
| 16, 18M | N ₂ + H + M → NH ₃ + M (1) | | ΔH (298) = -449 kJ/mol | |
| 17, M | N ₂ + M → NH ₂ + H + M (r) | | | |
| | Baulch, et al (1973) review | 200 - 3000 | $k_f = 1.2 \times 10^{-33} \exp(11200/T) \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$, M = Ar ? (a) (a) $k_f = k_{eq} k_r$ $k_r = 1.5 \times 10^{-8} \exp(-4240/T) \text{ (M = Ar)}$ 2 (b) (b) To be used when P(M) < 4 atm | |

This evaluation accepts the recommendation in the review of Baulch et al (1973)

REFERENCES

- Baulch, D. I., Drysdale, D. D., and Horne, D. G., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 2: Homogeneous Gas Phase Reactions of the H₂-N₂-O₂ System," (Butterworths, London, 1973)
- P. F. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No | Reaction/Reference | Temp Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncert Factor at 298K, notes |
|--------|--|-----------------|--|---------------------------------|
| 16, 21 | NH ₂ + N ₂ → NH ₃ + N (r) | | ΔH (298) = - 13 kJ/mol | |
| 17, 18 | NH ₃ + N → NH ₂ + N ₂ (r) | | | |
| | Baulch, et al (1973) review | 800 | k _f = < 10 ⁻¹⁶ k _r = < 10 ⁻¹⁶ | approximate approximate |
| | | | k _f = K _{eq} k _r | |

No recommendation

REFERENCES

Baulch, D. L., Drysdale, D. D., and Horne, D. G., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 2: Homogeneous Gas Phase Reactions of the H₂-N₂-O₂ System," (Butterworths, London, 1973)

D. F. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No | Reaction/Reference | Temp Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncert Factor at 298K, notes |
|--------|---|--------------|--|---------------------------------|
| 17, 19 | NH ₃ + H ₂ O → NH ₂ + H ₂ O (f) | | ΔF (298) = - 50 kJ/mol | |
| 16, 22 | NH ₂ + H ₂ O → NH ₃ + OH (r) | | | |
| | *Smith, Zellner (1975) | 228-472 | k _f = 2.3 x 10 ⁻¹² exp(-800/T) | 1 25 |
| | Perry, Atkinson, Pitts (1976a) | 298-427 | k _f = 2.9 x 10 ⁻¹² exp(-860 ± 150/T) | |
| | Cox, Derwent, Holt (1975) | 300 | k _f = (1.2 ± 0.4) x 10 ⁻¹³ | |
| | Hack, et al (1974) | 298-669 | k _f = 5.3 ± 0.2 x 10 ⁻¹² exp(-920/T) | |
| | Stuhl (1973a) | 258 | k _f = 1.5 x 10 ⁻¹³ | |
| | Kurylo (1973) | 298 | k _f = 4.1 x 10 ⁻¹⁴ | |
| | Gordon, Mulac (1975) | 418 | k _f = 4.3 ± 0.5 x 10 ⁻¹³ | |
| | Baulch, et al (1973) review | | k _r - no data, no recommendation | |

This evaluation accepts the results of the low temperature study of Smith and Zellner (1975). The results of Perry et al (1976a) and the room temperature result of Stuhl (1973a) are in good agreement

REFERENCES

- Baulch, D. L., Drysdale, D. D., and Horne, D. G., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 2: Homogeneous Gas Phase Reactions of the H₂-N₂-O₂ System," (Butterworths, London, 1973)
- Cox, R. A., Derwent, P. G., and Holt, P. M., "The Photo-oxidation of Ammonia in the Presence of NO and NO₂," *Chemosphere*, No. 4, 201-205 (1975)
- Gordon, S., and Mulac, W. A., "Reaction of the OH(X²Π) Radical Produced by the Pulse Radiolysis of Water Vapor," *Int. J. Chem. Kinet.*, Symp. No. 1, 285-299 (1975)
- Hack, W., Foyermann, K., and Wagner, H. Gg., "Reaktionen des Hydroxylradikals mit Ammoniak und Hydrazin in der gasphase," *Ber. Bunsenges. Physik. Chem.* 78, 386-391 (1974)
- Kurylo, M. J., "Kinetics of the Reactions OH(v = 0) + NH₃ → H₂O + NH₂ and OH(v = 0) + H₂ → H₂O + H₂ at 298°K," *Chem. Phys. Lett.* 23, 467-471 (1973)
- Perry, R. A., Atkinson, R., and Pitts, J. N., Jr., "Rate Constants for the Reactions OH + H₂S → H₂O + SH and OH + NH₃ → H₂O + NH₂ over the Temperature Range 297-427°K," *J. Chem. Phys.* 63, 3237-3239 (1976a)
- Smith, I. W. M., and Zellner, R., "Rate Measurements of Reactions of OH by

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No | Reaction/Reference | Temp Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncert Factor at 295K, notes |
|-------|--|-----------------|--|---------------------------------|
| 17,36 | NR ₂ + ClM → products Watson (1977) review | 670 | k < 5 × 10 ⁻¹⁶ | |

REFERENCES

Watson, P. Ic. "Rate Constants for Reactions of ClM_x of Atmospheric Interest," J. Phys. Chem. Ref. Data 6, 871-912 (1977)

R. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No | Reaction/Reference | Temp Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncert Factor at 298K, notes |
|--------|---|-----------------|--|---------------------------------|
| 17a.1a | N ₂ H ₄ + H → H ₂ + N ₂ H ₃ Stief, Payne (1976) | 228-400 | (9.87 ± 1.17) × 10 ⁻¹² exp(-1200 ± 52/T) | |

No recommendation

REFERENCES

Stief, L. J., and Payne, W. A., "Absolute Rate Parameters for the Reaction of Atomic Hydrogen with Hydrazine," J. Chem. Phys. **64**, 4892-4896 (1976)

R. F. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| Reaction/Reference | Tempo Range/K | Reaction Rate Constant $k/cm^3 \text{ molecule}^{-1} s^{-1}$ | Uncertainty Factor at 298K, notes |
|-------------------------------------|---------------|---|--------------------------------------|
| $H + H + M \rightarrow H_2 + M$ (1) | | $\Delta H(298) = -436 \text{ kJ/mol}$ | |
| $H_2 + M \rightarrow H + H + M$ (2) | | | |
| *Baulch, et al (1972) review | 300 | $k_f = 8.3 \times 10^{-33} \text{ cm}^6 \text{ molecule}^{-2} s^{-1}$ $M = H_2$ | 1.5 |
| | 1700-5000 | $= 1.8 \times 10^{-30} T^{-1}$ $M = Ar$ | 2 |
| | 2500-5000 | rel. efficiencies: $H_2(1.0)$, $Ar(0.25)$ $-d[H]/dt = 2k[H]^2[M]$ $k_f = 3.7 \times 10^{-10} \exp(-48300/T) \text{ cm}^3 \text{ molecule}^{-1} s^{-1}$, $M = Ar$ | 2 |

This evaluation accepts the recommendations in the review of Baulch et al (1972)

REFERENCES

Baulch, D. L., Drysdale, D. D., Horne, D. G., and Lloyd, A. G., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 1: Homogeneous Gas Phase Reactions of the H_2-O_2 System," (Butterworths, London, 1972)

P. F. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Temp. Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncerto. Factor at 298K, notes |
|--------|---|------------------|--|-----------------------------------|
| 18,19M | H + H ₂ O + M → H ₂ O + M (f) | | ΔH (298) = -495 kJ/mol | |
| 22, M | H ₂ O + M → H + H ₂ O + M (r) | | | |
| | Baulch, et al (1972) review | 1000-3000 | k _f = 6.1 x 10 ⁻²⁶ T ⁻² cm ⁶ molecule ⁻² s ⁻¹ , M = N ₂ | 2 |
| | | 2000-6000 | k _r = 5.8 x 10 ⁻⁹ exp(-52900/T) cm ³ molecule ⁻¹ s ⁻¹ M = N ₂ | 1.5 |
| | Zellner, Erler, Field (1977) | 230-300 | k _f = 4.3 x 10 ⁻²⁵ T ^{-2.6} M = He Rel off: He(1.0), Ar(1.5), N ₂ (3.2) | |

This evaluation accepts the recommendations in the review of Baulch et al (1972) for high temperatures.
For low temperatures use the new results of Zellner et al (1977)

REFERENCES

- Baulch, D. L., Drysdale, D. D., Horne, D. G., and Lloyd, A. G., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 1: Homogeneous Gas Phase Reactions of the H₂-O₂ System," (Butterworths, London, 1972)
- Zellner, R., Erler, K., and Field, D., "Kinetics of the Recombination Reaction OH + H + M → H₂O + M at Low Temperatures," Symp. Combust. 16th (Combustion Institute, Pittsburgh, 1977) 535-548

V. F. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Reaction/Reference
 Temp.
 Range/K
 Reaction Rate Constant
 $k/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$
 Uncert. Factor
 at 298K, notes

| No. | Reaction/Reference | Temp. Range/K | Reaction Rate Constant $k/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$ | Uncert. Factor at 298K, notes |
|-------|--|------------------|--|----------------------------------|
| 18,20 | $\text{H} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{H}_2\text{O}$ (12) | | $\Delta H (298) = -142 \text{ kJ/mol}$ | |
| 19,19 | $\text{H}_2 + \text{H}_2\text{O} \rightarrow \text{H} + \text{H}_2\text{O}$ (12) | | | |
| 18,20 | $\text{H} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{O}_2$ (2) | | $= -220 \text{ kJ/mol}$ | |
| 18,20 | $\text{H} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{O}$ (31) | | $= -213 \text{ kJ/mol}$ | |
| 1,22 | $\text{O} + \text{H}_2\text{O} \rightarrow \text{H} + \text{H}_2\text{O}$ (31) | | | |
| | CcDATA (1979) eval | | | |
| | | 252 | $k_{1f} = 3.2 \times 10^{-11}$ $k_2 = 1.4 \times 10^{-11}$ $k_{3f} = 9.4 \times 10^{-13}$ | 2.5 2.5 3 |
| | Hack, et al (1979) | 293 | $4.7 \times 10^{-11} (k = k_{1f} + k_2 + k_{3f})$ | |
| | Hack, et al (1978) | 293 | $k_{1f}/k = 0.69$ $k_2/k = 0.29$ $k_{3f}/k = 0.02$ | |
| | Baulch, et al (1972) review | 250-800 | $k_{1f} = 4.2 \times 10^{-10} \exp(-950/T)$ | |
| | | | $k_{1r} = k_{1f}/K_{eq} = 2.0 \times 10^{-11} \exp(-20200/T)$ | |
| | | 250-800 | $k_2 = 4.2 \times 10^{-11} \exp(-350/T)$ | |
| | | | $k_{2r} = k_{2f}/K_{eq} = 9.1 \times 10^{-11} \exp(-29100/T)$ k_{3f} and k_{3r} no recommendation | |

The preferred values are based on the overall rate reported by Hack et al (1979) and the branching ratio values of Hack et al (1978)

REFERENCES

Baulch, D. L., Drysdale, D. D., Horne, D. G., and Lloyd, A. C., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 1: Homogeneous Gas Phase Reactions of the $\text{H}_2\text{-O}_2$ System," (Butterworths, London, 1972)

C6DAVA(1979). Recommendations of the C6DATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.

Nack, W., Wagner, H. Gg., and Hoyermann, K., "Reaktionen von Wasserstoffatomen mit Hydroperoxylradikalen I. Bestimmung der spezifischen Geschwindigkeitskonstanten der Reaktionskanäle," Ber. Bunsenges. Phys. Chem. **82**, 713-719 (1978)

Nack, W., Preuss, A. W., Wagner, H. Gg., and Hoyermann, K., "Reaktionen von Wasserstoffatomen mit Hydroperoxylradikalen II. Bestimmung der Geschwindigkeitskonstanten der Bruttoreaktion," Ber. Bunsenges. Phys. Chem. **83**, 212-217 (1979)

R. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Reaction/Reference
 Temp.
 Range/K
 Reaction Rate Constant
 $k/cm^3 molecule^{-1} s^{-1}$
 Uncertainty Factor
 at 298K, notes

| | | | | | |
|-------|--|---------|--|---|-----|
| 18,23 | $H \cdot + H_2O_2 \rightarrow H_2O + HO_2 \cdot$ (1f) | | | $\Delta H (298) = -80 \text{ kJ/mol}$ | |
| 20,21 | $H_2O_2 \cdot + H_2 \rightarrow H \cdot + H_2O_2$ (1r) | | | | |
| 18,23 | $H \cdot + H_2O_2 \rightarrow HO \cdot + H_2O$ (2f) | | | -285 kJ/mol | |
| 19,22 | $HO \cdot + H_2 \rightarrow H \cdot + H_2O$ (2r) | | | | |
| | Stieglitz, Payne, Stief (1975) | 283-353 | | $k_{1f} \cdot k_{2f} = 5.2 \times 10^{-12} \exp(-1400 \pm 140/T)$ | 1.5 |
| | Gorse, Volman (1974) | 300 | | $k_{1f} = 3.1 \pm 0.8 \times 10^{-15}$ | |
| | | | | $k_{2f} = 5.7 \pm 1.4 \times 10^{-15}$ | |
| | Meagher, Heicklen (1975) | 298 | | $k_{2f}/k_{1f} = 1.3$ | |
| | Baulch, et al (1972) | 300-800 | | $k_{1f} = 2.8 \times 10^{-12} \exp(-1900/T)$ | |
| | | | | $k_{1r} = k_{1f}/K_{eq} = 1.2 \times 10^{-12} \exp(-9400/T)$ | |
| | | | | k_{2f} and k_{2r} : no recommendation | |

This evaluation accepts the results reported in Klemm et al (1975) for the overall rate of the forward reaction channels. Use the calculated expression of Baulch et al (1972) for k_{1r}

REFERENCES

Baulch, R. L., Drysdale, D. D., Horne, D. G., and Lloyd, A. G., "Evaluated Kinetic Data for High Temperature Reactions, Vol 1: Homogeneous Gas Phase Reactions of the H_2-O_2 System," (Butterworths, London, 1972)

Gorse, R. A., and Volman, D. H., "Photochemistry of the Gaseous Hydrogen Peroxide-Carbon Monoxide System II: Rate Constants for Hydroxyl Radical Reactions with Hydrocarbons and for Hydrogen Atom Reactions with Hydrogen Peroxide," J. Photochem. 3, 115-122 (1974)

Klemm, W. B., Payne, W. A., and Stief, L. J., "Absolute Rate Parameters for the Reaction of Atomic Hydrogen with H_2O_2 ," Int. J. Chem. Kinet., Symp. No. 1, 61-72 (1975)

Meagher, J. F., and Heicklen, J., "The Photolysis of Hydrogen Peroxide in the Presence of Carbon Monoxide," J. Photochem. 3, 455-466 (1975)

R. F. Hampson
 May 1978

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Reaction/Reference
Temp.
Range/K
Reaction Rate Constant
 $k/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$
Uncert. Factor
at 298K, notes

| No. | Reaction/Reference | Temp. Range/K | Reaction Rate Constant $k/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$ | Uncert. Factor at 298K, notes |
|-------|--|------------------|--|----------------------------------|
| 10,24 | $\text{H} + \text{HNO} \rightarrow \text{H}_2 + \text{NO} \quad (2)$ | | $\Delta H (298) = -227 \text{ kJ/mol}$ | |
| 9,21 | $\text{NO} + \text{H}_2 \rightarrow \text{H} + \text{HNO} \quad (r)$ | | | |
| | Hampson, et al (1973) review | 211-703 | $k_f > 5 \times 10^{-14}$ | 2 |
| | | 2000 | $k_f = 7 \times 10^{-12}$ | 2 |
| | Baulch, et al (1973) review | 300 | $10^{-13} < k < 10^{-12}$ | |
| | | 2000 | $k_f = 8 \times 10^{-12}$ | |
| | | 2000 | $k_r = k_f/K_{eq} = 5.3 \times 10^{-18}$ | |

This evaluation accepts the recommendations in the review of Hampson et al (1973)

REFERENCES

- Baulch, D. L., Drysdale, D. D., and Horne, D. G., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 2: Homogeneous Gas Phase Reactions of the $\text{H}_2\text{-N}_2\text{-O}_2$ System," (Butterworths, London, 1973)
- Hampson, R. F., (editor), "Survey of Photochemical and Rate Data for Twenty-Eight Reactions of Interest in Atmospheric Chemistry," J. Phys. Chem. Ref. Data 2, No. 2 pgs. 267-312 (1973). These are revised versions of data sheets originally distributed as NBS Reports 10592 and 10828.

R. F. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Uncertainty Factor
at 298K, notes

Reaction/Reference
Temp.
Range/K
Reaction Rate Constant
 $\text{L}/\text{cm}^3\text{-molecule}^{-1}\text{s}^{-1}$

No.

18.25 $\text{H} + \text{NO}_2 \rightarrow \text{products}$

Hampson, et al (1973) review

No data

No recommendation since there are no data

REFERENCES

Hampson, R. F., (editor), "Survey of Photochemical and Rate Data for Twenty-Eight Reactions of Interest in Atmospheric Chemistry," *J. Phys. Chem. Ref. Data* 2, No. 2 pgs. 267-312 (1973). These are revised versions of data sheets originally distributed as NBS Reports 10692 and 10828.

R. F. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL
KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Uncertainty Factor
at 298K, notes

Reaction/Reference
Temp.
Range/K
Reaction Rate Constant
k/cm³molecule⁻¹s⁻¹

No.

| | | | |
|-------|---------------------------------|-----|-------------------------|
| 18,26 | H + HNO ₃ → products | | |
| | *Chapman, Wayne (1974) | 300 | < 2 x 10 ⁻¹⁵ |
| | Hampson, et al (1973) review | 300 | < 1 x 10 ⁻¹³ |

Note that this is an upper limit only
Earlier results are discussed in the review of Hampson et al (1973)

REFERENCES

Chapman, C. J., and Wayne, R. P., "The Reaction of Atomic Oxygen and Hydrogen with Nitric Acid," *Int. J. Chem. Kinet.* **5**, 617-620 (1974)

Hampson, R. P., (editor), "Survey of Photochemical and Rate Data for Twenty-Eight Reactions of Interest in Atmospheric Chemistry," *J. Phys. Chem. Ref. Data* **2**, No. 2, 267-312 (1973). These are revised versions of data sheets originally distributed as NBS Reports 10692 and 10829.

R. P. Hampson
May 1976

PREPARED BY CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

CHEMICAL KINETICS DATA SURVEY

Uncert. Factor
at 298K, notes

Reaction/Reference Temp.
Range/K k/cm³molecule⁻¹s⁻¹

No.

19.20M H + SO₂ + M → HSO₂ + M

•Baulch, et al (1976) review

1660-2120

1.4 x 10⁻³² cm⁶molecule⁻²s⁻¹

1.5

This evaluation accepts the recommendation in the review of Baulch et al (1976)

REFERENCES

Baulch, D. L., Drysdale, D. D., Duxbury, J., and Grant, S. J., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 3: Homogeneous Gas Phase Reactions of the O₂-O₃ System, the CO-O₂-H₂ System, and of Sulphur-Containing Species," (Butterworths, London, 1976)

E. F. Hampson
May 1978

**CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS**

| No. | Reaction/Reference | Temp. Range/K | Reaction Rate Constant $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | ΔH (298) = - 87 kJ/mol | Uncert. Factor at 258K, notes |
|---------|--|------------------|--|--------------------------------|----------------------------------|
| 10, 31 | $\text{H} + \text{HS} \rightarrow \text{H}_2 + \text{S}$ (f) | | | | 1.5 |
| 21, 26a | $\text{H}_2 + \text{S} \rightarrow \text{H} + \text{HS}$ (r) | | | | 1.5 (a) |
| | *Bauch, et al (1976) review | 298 | $k_f = 2.5 \times 10^{-11}$ $k_r = 2.2 \times 10^{-25}$ (a) $k_r = k_f/K_{eq}$ | | |
| | Cupitt, Glass (1975) | 295 | $k_f = 2.5 \pm 0.8 \times 10^{-11}$ | | |

This evaluation accepts the recommendation in the review of Baulch et al (1976) which is confirmed by the results of Cupitt and Glass (1975)

REFERENCES

- Baulch, D. L., Drysdale, D. D., Duxbury, J., and Grant, S. J., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 3: Homogeneous Gas Phase Reactions of the O_2-O_3 System, the $CO-C_2H_2$ System, and of Sulphur-Containing Species," (Butterworths, London, 1976)
- R. F. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY
 PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Temp. Range/K | Reaction Rate Constant | | Uncertainty Factor at 298K, notes |
|-------|---|------------------|-------------------------------------|-------------------------------|--------------------------------------|
| | | | $k/cm^3 molecule^{-1} s^{-1}$ | $k/cm^3 molecule^{-1} s^{-1}$ | |
| 18,32 | $H + H_2S \rightarrow H_2 + HS$ Kurylo, Peterson, Braun (1971) | 190-464 | $1.29 \times 10^{-11} \exp(-860/T)$ | 51 kJ/mol | 1.5 |

This evaluation accepts the results of the temperature dependent study by Kurylo et al (1971).
 This result was also accepted in the Baulch et al (1976) review

REFERENCES

- Baulch, D. L., Drysdale, D. D., Duxbury, J., and Grant, S. J., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 3: Homogeneous Gas Phase Reactions of the O_2 - C_3 System, The CO - O_2 - H_2 System, and of Sulphur-Containing Species," (Butterworths, London, 1976)
- Kurylo, M. J., Peterson, M. C., and Braun, W., "Absolute Rate of the Reaction $H + H_2S \rightarrow H_2 + HS$," J. Chem. Phys. **54**, 943-946 (1971)
- R. F. Wampson
 May 1978

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Reaction/Reference Temp
Range/K Reaction Rate Constant
k/cm³ molecule⁻¹ s⁻¹ Uncertainty Factor
at 298K, notes

10.100 H + C₂H₅ → CH₃ + H₂ 300 ΔH (298) = - 40 kJ/mol
Baulch, et al (1976) review 2.2 x 10⁻¹⁴ 1.5

This evaluation accepts the recommendation in the review of Baulch et al (1976)

REFERENCES

Baulch, D. L., Drysdale, D. L., Duxbury, J. O. and Grant, S. J., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 3: Homogeneous Gas Phase Reactions of the O₂-C₃ System, the C₂H₂-H₂ System, and of Sulphur-Containing Species," (Butterworths, London, 1976)

F. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Tempo Range/K | Reaction Rate Constant $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | Uncert. Factor at 298K, notes |
|-------|---|------------------|--|----------------------------------|
| | | | | |
| 18,37 | H + CCl ₄ → HCl + CCl ₃ Watson (1977) review | 299 | $\Delta H (298) = -174 \text{ kJ/mol}$ 5.7×10^{-11} | 1.3 |

This evaluation accepts the recommendation in the Watson (1977) review

REFERENCES

Watson, R. L., "Rate Constants for Reactions of CCl₄ of Atmospheric Interest," J. Phys. Chem. Ref. Data 6, 871-918 (1977)

R. F. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Uncert. Factor
at 298K, notes

| No. | Reaction/Reference | Temp. Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | | Uncert. Factor at 298K, notes |
|-------|--|------------------|--|--|----------------------------------|
| | | | | | |
| 18.42 | H + NOCl - HCl + NO Ragner, et al (1976a) | 255-461 | ΔH (298) = -272 kJ/mol | 7.6 x 10 ⁻¹¹ exp(-457 ± 72/T) | |

These are the only temperature dependent results reported - no recommendation

REFERENCES

Wagner, K. G., Welzbacher, U., and Zellner, R., "Rate Measurements for
the Reactions H + NO₂ -> OH + NO and H + NOCl -> HCl + NO
by Lyman-α Fluorescence," *Ber. Bunsenges. Phys. Chem.* **80**,
1023-1027 (1976)

R. F. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Reaction/Reference
Tempo
Range/K

Reaction Rate Constant
k/cm³molecule⁻¹s⁻¹

Uncertainty Factor
at 298K, notes

| No. | Reaction/Reference | Tempo Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncertainty Factor at 298K, notes |
|-------|--------------------------------|------------------|--|--------------------------------------|
| | | | | |
| 10.44 | H + Cl ₂ → HCl + Cl | | ΔH (298) = -189 kJ/mol | |
| | This survey | 250-700 | 1.46 × 10 ⁻¹⁰ exp(-593/T) | 1.3 |
| | Bemand, Clyne (1977) | 300-730 | (1.41 ± 0.24) × 10 ⁻¹⁰ exp(-575 ± 65/T) | |
| | Wagner, et al (1976) | 252-458 | (1.44 ± 0.28) × 10 ⁻¹⁰ exp(-600 ± 70/T) | |
| | Ambidge, et al (1976) | 292-434 | (7.6 ± 2.2) × 10 ⁻¹¹ exp(-714 ± 100/T) | |

The recommended expression is based on the data reported by Bemand and Clyne (1977) and by Wagner et al (1976) which are in good agreement

REFERENCES

- Ambidge, P. F., Bradley, J. N., and Whytock, D. A., "Kinetic Study of the Reaction of Hydrogen Atoms with Molecular Chlorine," *J. Chem. Soc. Faraday Trans. I* **72**, 1157-1164 (1976)
- Bemand, P. F., and Clyne, M. A., "Atomic Resonance Fluorescence for Rate Constants of Rapid Bimolecular Reactions. Part 6a-Hydrogen Atom Reactions: H + Cl₂ from 300 to 730K and H + NO₂ at 298K," *J. Chem. Soc. Faraday Trans. II* **73**, 394-405 (1977)
- Wagner, H. G., Welzacher, U., and Zellner, P., "Rate Measurements for the Reaction H + Cl₂ → HCl + Cl by Lyman-α Fluorescence," *Ber. Bunsenges. Phys. Chem.* **80**, 502-908 (1976)

P. F. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Reaction/Reference

Tempo
Reaction Rate Constant

Range/K

Uncert. Factor
at 298K, notes

No.

| | | | | | |
|--------|---------------------------------|---------|--|-----------|------|
| 18,454 | $H + CO \rightarrow H_2 + CO_2$ | 298-773 | $AR(298) = -70 \text{ kJ/mol}$ $2.0 \times 10^{-33} \exp(-850/T) \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$ | $M = H_2$ | 1.03 |
| | Baulch, et al (1976) review | | | | |

This evaluation accepts the recommendation in the review of Baulch et al (1976)

REFERENCES

Baulch, D. L., Drysdale, D. D., Duxbury, J., and Grant, S. J., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 3: Homogeneous Gas Phase Reactions of the C_2-C_3 System, the $CO-C_2-H_2$ System, and of Sulphur-Containing Species," (Butterworths, London, 1976)

Y. F. Hampson
May 1978

Uncerto. Factor
at 298K, notes

| No. | Reaction/Reference | Tempo Range/K | Reaction rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncertainty Factor at 298K, notes |
|--------|--|------------------|--|--------------------------------------|
| 180.48 | H + CH ₂ O → H ₂ + CH ₃ O | 257 | 5.4 × 10 ⁻¹⁴ | |
| | Pidley, et al (1972) | 257-652 | 2.2 × 10 ⁻¹¹ exp(-1890/T) | |
| | Westenberg, deHaas (1972b) | | | |

NO recommendation

REFERENCES

- Ridley, E. A., Davenport, J. A., Stief, L. J., and Welge, K. W., "Absolute Rate Constant for the Reaction $H + H_2CO$," *J. Chem. Phys.* **51**, 520-523 (1972)
- Westenberg, A. A., and deHaas, N., "Measurement of the Rate Constant for $H + H_2CO \rightarrow H_2 + HCO$ at 297-652°K," *J. Phys. Chem.* **76**, 2213-2214 (1972b)

PO. F. Hampton
MAY 1978

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS
Reaction/Reference **Temp** **Reaction Rate Constant** **Uncertainty Factor**
Range/K **k/cm³molecule⁻¹s⁻¹** **at 298K, notes**

| No. | Reaction/Reference | Temp Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncertainty Factor at 298K, notes |
|-------|--|-----------------|---|--------------------------------------|
| 18.53 | B + CH ₃ OOH - CH ₃ O + H ₂ O (a) - CH ₃ O ₂ + H ₂ (b) - CH ₂ OOH + H ₂ (c) Slemr, Varneck (1977) | 250-358 | ΔH (298) = -314 kJ/mol = - 80 kJ/mol k = (2.8 ± 0.9) × 10 ⁻¹³ exp(-930 ± 95/T) k _a /k = 0.43 ± 0.07 k _b /k = 0.52 ± 0.07 k _c /k = 0.05 | overall rate const |

only reported value - no recommendation

REFERENCES

Slemr, F., and Varneck, P., "Kinetics of the Reaction of Atomic Hydrogen with Methylhydroperoxide," *Int. J. Chem. Kinet.* **9**, 267-282 (1977)

F. F. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS
Reaction/Reference Temp. Reaction Rate Constant
Range/K k/cm³molecule⁻¹s⁻¹

Uncertainty Factor
at 298K, notes

| No. | Reaction/Reference | Temp. Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncertainty Factor at 298K, notes |
|-------|--|------------------|--|--------------------------------------|
| 18.64 | H + CH ₃ Cl → HCl + CH ₃ Vestenberg, deHaas (1975a) | 500-800 | ΔH (298) = - 83 kJ/mol 6.2 × 10 ⁻¹¹ exp(-4650/T) | |

No recommendation

REFERENCES

Vestenberg, A. A., and deHaas, M., "Rates of H + CH₃X Reactions," J. Chem. Phys. **62**, 3321-3325 (1975a)
R. F. Hampson
May 1976

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Uncertainty Factor
 at 298K, notes

Reaction/Reference
 Tempo
 Range/K
 Reaction Rate Constant
 k/cm³molecule⁻¹s⁻¹

No.

| | | |
|-------|---|--|
| 19.19 | • H ₂ - H ₂ • O ₂ (f) | ΔH (298) = - 78 kJ/mol |
| 4.21 | O ₂ • H ₂ - H ₂ • HO (r) | |
| | Baulch, et al (1972) review | no recommendation given for k _f or k _r |

No recommendation

REFERENCES

Baulch, D. L., Drysdale, D. D., Horne, D. G., and Lloyd, A. G., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 1: Homogeneous Gas Phase Reactions of the H₂-O₂ System," (Butterworths, London, 1972)

L. F. Hampson
 May 1978

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Uncerto. Factor
at 298K, notes

| No. | Reaction/Reference | Tempo Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncerto. Factor at 298K, notes |
|-------|--|------------------|--|-----------------------------------|
| | | | | |
| 19,19 | H ₂ + H ₂ O → H ₂ O ⁺ + H ₂ (2) | | ΔH (298) = - 71 kJ/mol | |
| 1,22 | C + H ₂ O → H ₂ + CO (r) | | | 1e25 |
| | WUSA (1979) eval | | | 1e5 |
| | CODATA (1979) eval | 200-300 | k _f = 1 x 10 ⁻¹¹ exp(-(500400)/T) | |
| | Westenberg, deHaas (1973b) | 258 | k _f = 1.8 x 10 ⁻¹² | |
| | McKenzie, et al (1973) | 300 | k _f = 2.3 x 10 ⁻¹² | |
| | Clyne, Down (1974) | 258 | k _f = 2.1 ± 0.5 x 10 ⁻¹² | |
| | Trainer, von Rosenberg (1974) | 300 | k _f = 1.4 ± 0.2 x 10 ⁻¹² | |
| | Baulch, et al (1972) review | 300-2000 | k _f = 2.1 ± 0.2 x 10 ⁻¹² | |
| | Rawlins, Gardiner (1974) | 300-2000 | k _f = 1.0 x 10 ⁻¹¹ exp(-550/T) | |
| | | 300-2000 | k _f = 1.1 x 10 ⁻¹⁰ exp(-9240/T) | |
| | | 1500-2000 | k _f = 9.1 x 10 ⁻¹¹ exp(-3500/T) | |

This value is based on a re-evaluation of the recent measurements of Westenberg and deHaas (1973b), McKenzie et al (1973), Clyne and Down (1974) and Trainer and von Rosenberg (1974). There are no T dependence data around room temperature

REFERENCES

- Baulch, D. L., Drysdale, D. D., Horne, D. G., and Lloyd, A. C., "Evaluated Kinetic Data for High Temperature Reactions, Vol. I: Homogeneous Gas Phase Reactions of the H₂-O₂ System," (Butterworths, London, 1972)
- Clyne, M. A. A., and Down, S., "Kinetic Behaviour of CH X²Π and A²Σ⁺ using Molecular Resonance Fluorescence Spectrometry," J. Chem. Soc. Faraday Trans. II 70, 252-266 (1974)
- CODATA(1979). Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.
- McKenzie, A., Mulcahy, M. F. R., and Steven, J. R., "Kinetics of Decay of Hydroxyl Radicals at Low Pressure," J. Chem. Phys. 59, 3244-3254 (1973)

NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," R. De Hudson and E. L. Reed, Editors, Dec. 1975 (report of the June 1979 Barbers Ferry Workshop).

Nailling, W. T., and Gardiner, W. C., Jr., "Rate Constant of $\text{OH} + \text{OH} = \text{H}_2\text{O} + \text{O}$ from 1500 to 2000 K," J. Chem. Phys. **60**, 4676-4681 (1974)

Trainer, D. W., and von Rosenberg, C. W., Jr., "Flash Photolysis Study of the Gas Phase Recombination of Hydroxyl Radicals," J. Chem. Phys. **61**, 1010-1015 (1974)

Veenberg, A. A., and deHaas, N., "Rate of the Reaction $\text{OH} + \text{OH} = \text{H}_2\text{O} + \text{O}$," J. Chem. Phys. **53**, 4066-4071 (1973b)

R. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No | Reaction/Reference | Temp Range/K | Reaction Rate Constant k/cm ³ molecule ⁻² s ⁻¹ | Uncert Factor at 298K, notes |
|---------|---|-----------------|--|---------------------------------|
| 19, 19M | H ⁺ + H ₂ O → H ₂ O ⁺ + M (f) | | ΔH (298) = -214 kJ/mol | |
| 23, M | H ₂ O ₂ + M → H ₂ O + H ₂ O (r) | | k _f = (2.5 ± 1.3) × 10 ⁻³¹ (T/300) ^{-0.8} , M = N ₂ | |
| | NASA (1979) eval | 200-300 | k _{f,∞} = (3.0 ± 1.5) × 10 ⁻¹¹ (T/300) ^{-1.41} cm ³ molecule ⁻¹ s ⁻¹ | |
| | CODATA (1979) eval | 298 | k _f = 6.5 × 10 ⁻³¹ , M = N ₂ | 2 |
| | Trainer, von Rosenberg (1974) | 300 | k _f = 2.5 ± 0.3 × 10 ⁻³¹ M = N ₂ | 2 |
| | Baulch, et al (1972) review | 700-1500 | k _f = 2.5 × 10 ⁻³³ exp(+2550/T), M = N ₂ | 2 |
| | | | k _r = 2.0 × 10 ⁻⁷ exp(-22900/T) cm ³ molecule ⁻¹ s ⁻¹ , M = N ₂ ; k _f = k _r ^{eq} | 2 |

REFERENCES

- Baulch, D. L., Drysdale, D. D., Horne, D. G., and Lloyd, A. C., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 1: Homogeneous Gas Phase Reactions of the H₂-O₂ System," (Butterworths, London, 1972)
- CODATA(1979). Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.
- NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA SP 1049 "The Stratosphere: Present and Future," R. D. Hudson and E. I. Reed, Editors, Dec. 1975 (report of the June 1975 Harpers Ferry Workshop).
- Trainer, D. W., and von Rosenberg, C. W., Jr., "Flash Photolysis Study of the Gas Phase Recombination of Hydroxyl Radicals," J. Chem. Phys. **51**, 1010-1015 (1974)
- R. F. Harpison
June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Temp. Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | | Uncerto. Factor at 298K, notes |
|-------|--|------------------|---|----------------|-----------------------------------|
| | | | | | |
| 19,20 | H ₂ + H ₂ O ₂ → H ₂ O + O ₂ | | ΔH (298) = -283 kJ/mol | | |
| | NASA (1979) eval | 200-300 | 4 × 10 ⁻¹¹ | exp((0±250)/T) | 2 |
| | CODATA (1979) eval | 298 | 3.5 × 10 ⁻¹¹ | | 3 |
| | Chang, Kaufman (1978) | 295 | 2-3 × 10 ⁻¹¹ | | |
| | DeMore (1979) | 298 | ~ 1 × 10 ⁻¹⁰ | | |
| | Back, et al (1978) | 293 | (3 ± 1) × 10 ⁻¹¹ | | |
| | Burrows, Harris, Thrush (1977) | 293 | 5.1 × 10 ⁻¹¹ | | (a) |
| | | | (a) Based on k(H ₂ + H ₂ O ₂) = 8 × 10 ⁻¹³ | | |
| | Rocheadell, et al (1972) | 300 | 2 × 10 ⁻¹⁰ | | |
| | DeMore, Tschuikow-Poux (1974) | 300 | ~ 1 × 10 ⁻¹⁰ | | |

The recommended value is derived from the upper limit of Chang and Kaufman (1978), the measurement of Back et al (1978), and the ratio measurement (relative to OH + H₂O₂) by Burrows et al (1977) and is within the experimental accuracy of all three studies, although it is not compatible with the value of 1-2 × 10⁻¹⁰ derived from rate constant ratios in steady state O₃ photolysis experiments by DeMore and Tschuikow-Poux (1974) and DeMore (1979)

REFERENCES

Burrows, J. P., Harris, G. W., and Thrush, B. A., "Rates of Reaction of H₂ with H₂O₂ and O₃ studied by Laser Magnetic Resonance," *Nature* **267**, 233-234 (1977)

Chana, J. S., and Kaufman, F., "Upper Bound and Probable Value of the Rate Constant of the Reaction OH + H₂O₂ → H₂O + O₂," *J. Phys. Chem.* **82**, 1683-1687 (1978)

CODATA(1979). Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the *Journal of Physical and Chemical Reference Data*.

DeMore, W. B., "Reaction of H₂O₂ with O₃ and the Effect of Water Vapor on H₂O₂ Kinetics," *J. Phys. Chem.* **83**, 1113-1118 (1979)

DeMore, W. B., and Tschuikow-Poux, E., "Temperature Dependence of the Reactions of OH and H₂O₂ with O₃," *J. Phys. Chem.* **78**, 1447-1451 (1974)

Back, W., Preuss, A. V., and Wagner, H. G. G. "Messung der Geschwindigkeit der Reaktion von OH- und HO₂-Radikalen mit Halogenen der Laser-Magnetischen Resonanz," *Bere. Bunsenges. Phys. Chem.* **82**, 1167-1171 (1978)

Wohlschlagel, G. J., Ghersey, J. A., and Ogren, P. J., "Absorption Spectrum and Reaction Kinetics of HO₂ Radical in the Gas Phase," *J. Chem. Phys.* **56**, 4426-4432 (1972)

NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," R. D. Hudson and E. L. Reed, Editors, Dec. 1979 (report of the June 1975 Harpers Ferry Workshop).

R. F. Hampson
June 1979

AD-A091 631

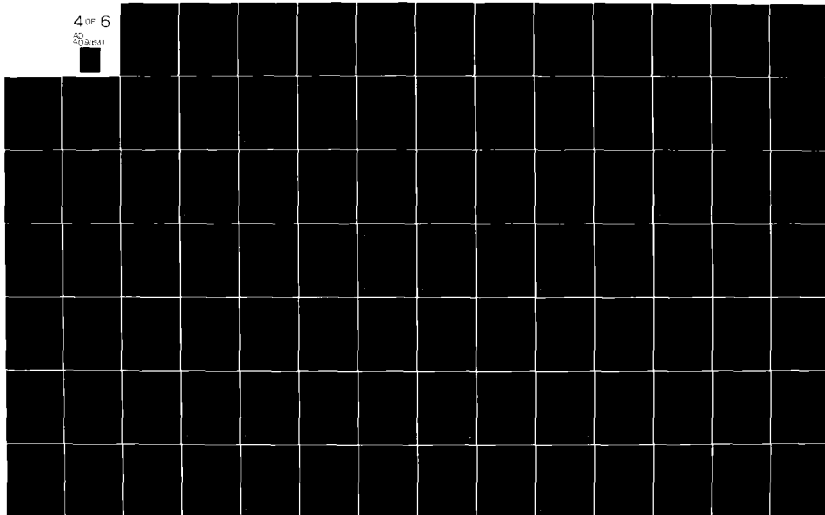
NATIONAL BUREAU OF STANDARDS WASHINGTON DC CHEMICAL --ETC F/G 4/1
CHEMICAL KINETIC AND PHOTOCHEMICAL DATA SHEETS FOR ATMOSPHERIC --ETC
APR 80 R F HAMPSON DOT-FA79WAI-005 NL

UNCLASSIFIED

FAA/EE-80-17

4 OF 6

50
CLASS



CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEN

Reaction Rate Constant

Reaction/Reference

you

This reaction is new to the NASA Tables. The recommendation is based on three T dependence studies which

REFERENCES

- Atkinson, R.: Hansen, D. A., and Pitts, J. N., Jr., "Rate Constants for the

Heulch. D. L., Devsdale, D. D., Horne, D. G., and Lloyd, A. Co. "Evaluated

Kinetic Data for High Temperature Reactions. Vol. 1: Homogeneous

Gas Phase Reactions of the H_2-O_2 System," (Butterworths, London, 1972)

- CODATA(1979). Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.
- Gardiner, W. Co. Jr., Mallard, W. G., and Owen, J. B., "Rate Constant of $\text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H}$ from 1350 to 1600 K," *J. Chem. Phys.* **59**, 2290-2295 (1974)
- Greiner, M. P., "Hydroxyl Radical Kinetics by Kinetic Spectroscopy. V. Reactions with H_2 and CO in the Range 300-500 K," *J. Chem. Phys.* **51**, 5049-5051 (1969)
- Hampson, R. F., and Garvin, D., "Reaction Rate and Photochemical Data for Atmospheric Chemistry-1977" U.S. National Bureau of Standards Special Publication 513, May 1978.
- NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," W. D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the June 1979 Harpers Ferry Workshop).
- Overend, R., Paraskevopoulos, M., and Cvitanović, P. J., "Rates of OH Radical Reactions. I. Reactions with H_2 , CH_4 , C_2H_6 , and C_3H_8 at 295 K," *Can. J. Chem.* **53**, 3374-3382 (1975)
- Smith, I. W. M., and Zellner, R., "Rate Measurements of Reactions of OH by Resonance Absorption. Part 3. Reactions of OH with H_2 , D_2 , Hydrogen and Deuterium Halides," *J. Chem. Soc., Faraday Trans. II* **70**, 1045-1056 (1974a)
- Stuhl, F., and Nix, R., "Pulsed Vacuum-uv Photochemical Study of Reactions of OH with H_2 , D_2 , and CO Using a Resonance-Fluorescent Detection Method," *J. Chem. Phys.* **57**, 3671-3677 (1972)
- Trainor, D. W., and von Rosenberg, C. W., Jr., "Energy Partitioning in the Products of Elementary Reactions Involving OH -Radicals," *Symp. Combust.* 15th (Combustion Institute, Pittsburgh, 1975) 755-764
- Vandoren, J., Peeters, J., and Van Tiggelen, P. J., "Rate Constant of the Elementary Reaction of Carbon Monoxide with Hydroxyl Radical," *Symp. Combust.* 15th (Combustion Institute, Pittsburgh, 1975) 745-752
- Vestenberg, A. A., and deHaas, M., "Rates of $\text{CO} + \text{OH}$ and $\text{H}_2 + \text{OH}$ over an Extended Temperature Range," *J. Chem. Phys.* **58**, 4061-4065 (1973a)
- Y. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY
 PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Uncert. Factor
 at 258K, notes

Reaction/Reference
 Temp.
 Range/K
 Reaction Rate Constant
 $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

No.

19.21D $\text{H}^+ + \text{D}_2 \rightarrow \text{HD} + \text{D}$

Smith, Zellner (1974a)

210-460

$1.25 \times 10^{-11} \exp(-2590/T)$

These are the only temperature dependent results reported. The room temperature value is in good agreement with two earlier studies

REFERENCES

Smith, I. W. No. and Zellner, R., "Rate Measurements of Reactions of OH
 by Resonance Absorption. Part 3. Reactions of OH with H_2 , D_2 , Hydrogen
 and Deuterium Halides," J. Chem. Soc., Faraday Trans. II **70**, 1045-1056 (1974a)

R. F. Hampson
 May 1976

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Reaction/Reference
Temp.
Range/K
Reaction Rate Constant
 $k/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$
Uncert. Factor
at 298K, notes

| No. | Reaction/Reference | Temp. Range/K | Reaction Rate Constant $k/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$ | Uncert. Factor at 298K, notes |
|-------|---|------------------|--|----------------------------------|
| 19,23 | $\text{H}_2 + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{H}_2\text{O}_2$ (r) | | $\Delta H(298) = -143 \text{ kJ/mol}$ | |
| 20,22 | $\text{H}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{H}_2\text{O}_2$ (r) | | | |
| | NASA (1979) eval | 200-300 | $k_1 = 1 \times 10^{-11} \exp(-(750+350)/T)$ | 2 |
| | CBDATA (1979) eval | 200-700 | $k_2 = 7.6 \times 10^{-12} \exp(-(670+200)/T)$ | 2 |
| | Rack, et al (1975) | 298-670 | $k_1 = 8.0 \times 10^{-12} \exp(-670/T)$ | |
| | Greiner (1968) | 300-458 | $k_1 = 4.1 \times 10^{-13} T^{1/2} \exp(-600/T)$ | |
| | Harris, Pitts (1979) | 298 | $k_1 = 6.8 \times 10^{-13}$ | |
| | Baulch, et al (1972) review | 300-800 | $k_1 = k_2/K_{eq} = 4.7 \times 10^{-11} \exp(-16500/T)$ | |
| | Gorse, Volman (1972) | 300 | $k_1/k(\text{H}_2 + \text{C}_6) = 8.1$ | |
| | Meagher, Heicklen (1974) | 258 | $k_1/k(\text{H}_2 + \text{C}_6) = 4.1$ | |

This value is a composite of a recent Rack et al (1975) measurement of $8 \times 10^{-12} \exp(-670/T) \text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$ with earlier work of Greiner (1968). Although the two studies are in relatively good agreement, there are reasons to question both determinations. The Greiner work involved a large temperature increase due to absorption of flash energy. The Rack et al study used radical densities of $3 \times 10^{13} \text{cm}^{-3}$ and may have been complicated by the back reaction between the product H_2O_2 and residual NO from the OH formation step. The new value for $k(\text{H}_2\text{O}_2 + \text{NO})$ of 8×10^{-12} implies a very rapid reversion. Additional studies are needed. The A-factor seems unreasonably high for this type of reaction. Harris and Pitts (1979) confirm our room temperature recommendation. Preliminary data by Keyser, however, is about a factor of three higher. This reaction clearly requires additional work, especially on the T dependence.

REFERENCES

- Baulch, D. L., Drysdale, D. D., Horne, D. G., and Lloyd, A. C., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 1: Homogeneous Gas Phase Reactions of the $\text{H}_2\text{-O}_2$ System," (Butterworths, London, 1972)
- CBDATA(1979), Recommendations of the CBDATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.
- Gorse, V. A., and Volman, D. H., "Photochemistry of the Gaseous Hydrogen Peroxide-Carbon Monoxide System: Rate Constants for Hydroxyl Radical Reactions with Hydrogen Peroxide and Isobutane by Competitive Kinetics," J. Photochem. 1, 1-10 (1972)

- Graimer, M. D., "Hydroxyl Radical Kinetics by Kinetic Spectroscopy. III. Reactions with H_2O_2 in the Range 300-450°K," *J. Phys. Chem.* **72**, 406-410 (1968)
- Hack, W., Heyermann, L., and Wagner, H. G., "The Reaction $HO + H_2O_2 \rightarrow HO_2 + OH$ with $OH + H_2O_2 \rightarrow H_2O + H_2O_2$ as an HO_2 -Source," *Int. J. Chem. Kinet.*, Symp. No. 1, 329-339 (1975)
- Harris, G. W., and Pitts, J. N. Jr., "Rate Constant for the Reaction of OH Radicals with Hydrogen Peroxide at 298 K," *J. Chem. Phys.* **70**, 2581-2582 (1979)
- Keyser, L., Manuscript in preparation, Jet Propulsion Laboratory, Pasadena, CA, 91003 (1979)
- Neagher, J. F., and Heicklen, J., "The Photolysis of Hydrogen Peroxide in the Presence of Carbon Monoxide," *J. Photochem.* **3**, 455-466 (1975)
- NASA (1979), Recommendations of the NASA Panel for Data Evaluation, published in NASA RP-1049 "The Stratosphere: Present and Future," R. D. Hudson and E. L. Reed, Editors, Dec. 1979 (report of the June 1979 Harpers Ferry Workshop).
- R. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Uncert. Factor
at 298K, notes

Reaction Rate Constant
k/cm³molecule⁻¹s⁻¹

Temp.
Range/K

Reaction/Reference

No.

| | | | | |
|-------|--|-----------|--|---|
| 19,24 | H ₂ + HNO → H ₂ O + NO (1) | | ΔH (298) = -291 kJ/mol | |
| 9,22 | NO + H ₂ O → H ₂ + HNO (2) | | | |
| | Hampson, et al (1973) review | 1600-2100 | k ₂ = 7 x 10 ⁻¹¹ | 5 |
| | Baulch, et al (1973) review | 2000 | k ₂ = 6 x 10 ⁻¹¹ | |
| | | | k _r = k ₂ /K _{eq} = 4 x 10 ⁻¹⁸ (corrected) | |

This evaluation accepts the temperature - independent recommendation in the review of Hampson et al (1973)

REFERENCES

- Baulch, D. L., Drysdale, D. D., and Horne, D. G., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 2: Homogeneous Gas Phase Reactions of the H₂-N₂-O₂ System," (Butterworths, London, 1973)
- Hampson, R. F., (editor), "Survey of Photochemical and Rate Data for Twenty-Eight Reactions of Interest in Atmospheric Chemistry," J. Phys. Chem. Ref. Data 2, No. 2, pgs 267-312 (1973). These are revised versions of data sheets originally distributed as NBS Reports 10692 and 10828.

R. F. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Tempo Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncert. Factor at 298K, notes |
|-------|---|------------------|--|----------------------------------|
| | | | | |
| 19,25 | NO + HNO ₂ → H ₂ O + NO ₂ Cox, Derwent, Holt (1976) | 296 | AR (298) = -169 kJ/mol 6.6 x 10 ⁻¹² ref. rxn is NO + H ₂ → H ₂ O + H with k _{ref} = 7 x 10 ⁻¹⁵ k/k(NO + CO) = 15 ± 1 at 1 atm air | 1.5 |
| | Cox (1974) | 294 | | |

This evaluation accepts the results of Cox et al (1976) with error limits to encompass the value derived from the ratio reported in Cox (1974) and the value of k(NO + CO) at 1 atm air

REFERENCES

- Cox, R. A., "The Photolysis of Nitrous Acid in the Presence of Carbon Monoxide and Sulphur Dioxide," J. Photochem. 3, 291-304 (1974)
- Cox, R. A., Derwent, R. G., and Holt, P. M., "Relative Rate Constants for the Reactions of OH Radicals with H₂, CH₄, CO, NO and HONO at Atmospheric Pressure and 296 K," J. Chem. Soc., Faraday Trans. 1 72, 2031-2043 (1976)

R. F. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Uncertainty Factor
at 298K, notes

Reaction/Reference
Temp.
Range/K
Reaction Rate Constant
 $k/cm^3 \text{ molecule}^{-1} s^{-1}$

No.

| | | | | |
|-------|--|-------------------------------|---|------|
| 19,26 | $HO + HNO_3 \rightarrow H_2O + NO_2$ (1) | ΔH (298) = -75 kJ/mol | | |
| 11,22 | $HO_2 + H_2O \rightarrow HO + HNO_3$ (2) | | | |
| | NASA (1979) eval | | | |
| | CODATA (1979) eval | | | |
| | Smith, Zellner (1975) | 200-300 | $k_1 = 8.5 \times 10^{-14} \exp((0 \pm 100)/T)$ | 1.25 |
| | Margitan, et al (1975) | 240-470 | $k_1 = 8.5 \times 10^{-14} \exp((0 \pm 300)/T)$ | 1.25 |
| | Baulch, et al (1973) review | 240-406 | $k_1 = 8 \pm 2 \times 10^{-14}$ | |
| | | 270-470 | $k_1 = 8.9 \pm 1.3 \times 10^{-14}$ | |
| | | 300 | $k_1 = k_2/K_{eq} = 2.3 \times 10^{-26}$ | |

Recommended value is a simple average of the results reported by Smith and Zellner (1975) and Margitan et al (1975). A slightly lower value was recommended in NASA RP-1010 based only on the results of Smith and Zellner, considered as confirmed by the results of Margitan et al. Products are unknown--reaction may proceed by addition mechanism. The apparent A-factor is low for an abstraction reaction

REFERENCES

- Baulch, D. L., Drysdale, D. D., and Horne, D. G., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 2: Homogeneous Gas Phase Reactions of the H_2 - N_2 - O_2 System," (Butterworths, London, 1973)
- CODATA (1979), Recommendations of the CODATA Task Group on Chemical Kinetics, To be published in the Journal of Physical and Chemical Reference Data.
- Margitan, J. J., Kaufman, F., and Anderson, J. G., "Kinetics of the Reaction $OH + HNO_3 \rightarrow H_2O + NO_2$," Int. J. Chem. Kinet., Symp. No. 1, 261-287 (1975)
- NASA RP-1010, "Chlorofluoromethanes and the Stratosphere"
- E. D. Budson, Editor, August 1977 This reference contains the NASA (1977) rate constant recommendations.

NASA (1979). Recommendations of the NASA Panel for Data Evaluation,
published in NASA RP 1049 "The Stratosphere: Present and Future."
R. D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the
June 1979 Harpers Ferry Workshop).
Smith, I. W. M., and Zellner, R. "Rate Measurements of Reactions of OH by
Resonance Absorption. IV. - Reactions of OH with NH_3 and HNO_3 ."
Int. J. Chem. Kinet., Symp. No. 1, 341-351 (1975)
R. P. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Temp. Range/° | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncert. Factor at 298K, notes |
|--------|---|------------------|--|----------------------------------|
| 19,26a | NO + NO ₂ NO ₂ - products | | | |
| | NASA (1979) eval | 298 | 5 x 10 ⁻¹³ | 10 |
| | CODATA (1979) eval | 298 | 1 x 10 ⁻¹³ | 10 |
| | Graham, Winer, Pitts (1978) | 255 | 43 x 10 ⁻¹² | |

Estimated by analogy with the Reaction OH + H₂O₂. This value is consistent with the upper limit reported by Graham, Winer and Pitts (1978)

REFERENCES

CODATA(1979). Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.

Graham, R. A., Winer, A. M., and Pitts, J. N. Jr., "Pressure and Temperature Dependence of the Unimolecular Recombination of NO₂NO₂," J. Chem. Phys. **68**, 4505-4510 (1978)

NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," R. D. Hudson and E. I. Reed, Editors, Dec. 1975 (report of the June 1975 Harpers Ferry Workshop).

R. F. Hampson
 June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No | Reaction/Reference | Temp. Range/K | Reaction Rate Constant $k/\text{cm}^6\text{molecule}^{-2}\text{s}^{-1}$ | Uncert. Factor at 298K, notes |
|--------|--|---------------|--|----------------------------------|
| 19,28N | $\text{Hd} + \text{Sd}_2 \rightarrow \text{H} + \text{HSd}_3 + \text{M}$ NASA (1979) eval | 200-300 | ΔH (298) = -223 kJ/mol $k = (3.0 \pm 0.5) \times 10^{-31} (T/300)^{-2.9 \pm 1}$, $M = \text{N}_2$ $k_{\infty} = (2.0 \pm 0.5) \times 10^{-12} (T/300)^{0 \pm 1}$ $\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$ $k = 3 \times 10^{-31} (T/300)^{-2.9}$, $M = \text{N}_2$ $k_{\infty} = 2 \times 10^{-12}$ $\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$ | 2 2.5 (a) |
| | CGDATA (1979) eval | 200-400 | | |
| | Davis, et al (1979) | 300 | $10^{13} \frac{k}{\text{M}}$ 0.75 ± 0.07 1.41 ± 0.08 2.16 ± 0.20 (a) Effective 2nd order rate constant in $\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$ Data also given for $M = \text{He}$ and Ar . Authors estimate value of 9×10^{-13} at 1 atm N_2 | (a) |
| | Harris, Wayne (1975) | 300 | $4.5 \pm 1.5 \times 10^{-31}$, $M = \text{Ar}$ $7.2 \pm 2.6 \times 10^{-31}$, $M = \text{N}_2$ $k/k(\text{Hd} + \text{Cd}) = 4 \pm 0.5$ | (c) |
| | Cox (1974) | 294 | (c) 2nd order rate constant, $[M] = 1$ atm. $\text{N}_2 + \text{C}_2$ see entry for $k(\text{Hd} + \text{Cd})$ | |
| | Gordon, Mulac (1975) | 435 | 1.2×10^{-12} $\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$ (2d order rate constant at 1 atm. H_2O vapor) | |
| | Castleman, Tang (1977) | 297 | 1.6×10^{-31} , $M = \text{N}_2$ $k/k(\text{Hd} + \text{Cd}) = 4.3$ | (d) |
| | Atkinson, Perry, Pitts (1976) | 298 | (d) Measured ratio of 2d order rate constants at 1 atm N_2 . Values for k given in paper assumed $k_{\text{ref}} = 1.5 \times 10^{-13}$ over entire pressure range. See entry for $k(\text{Hd} + \text{Cd})$ | (e) |
| | | | $10^{13} \frac{k}{\text{M}}$ 1.35 2.16 3.10 4.38 5.87 6.55 | (e) |
| | | | $P(\text{Ar})/\text{torr}$ 25 50 100 202 402 648 | |
| | | | (e) Effective 2nd order rate constant in $\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$ | |

See the discussion of the rate data for this reaction in the review by Zellner (1978)

REFERENCES

- Athinson, E., Perry, E. A., and Pitts, J. N., Jr., "Rate Constants for the Reactions of the OH Radical with NO_2 (M - Ar and N_2) and SO_2 (M - Ar)," *J. Chem. Phys.* **65**, 306-310 (1976)
- Castleman, A. W., Jr., and Tang, I. N., "Kinetics of the Association Reaction of SO_2 with the Hydroxyl Radical," *J. Photochem.* **6**, 349-354 (1977)
- CODATA(1979). Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.
- Cox, R. A., "The Photolysis of Nitrous Acid in the Presence of Carbon Monoxide and Sulphur Dioxide," *J. Photochem.* **3**, 291-304 (1974)
- Davis, D. D., Ravishankara, A. R., and Fischer, S., " SO_2 Oxidation via the Hydroxyl Radical: Atmospheric Fate of HSO_3 Radicals," *Geophys. Res. Lett.* **6**, 113-116 (1979)
- Gordon, S., and Mulaic, V. A., "Reaction of the $\text{CH}(\text{X}^2\Pi)$ Radical Produced by the Pulse Radiolysis of Water Vapor," *Int. J. Chem. Kinet.*, Sympo No. 1, 285-295 (1975)
- Harris, G. E., and Wayne, R. P., "Reaction of Hydroxyl Radicals with NO , NO_2 and SO_2 ," *J. Chem. Soc., Faraday Trans. I* **71**, 610-617 (1975)
- NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA EP 1049 "The Stratosphere: Present and Future," R. D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the June 1975 Harper Ferry Workshop).
- Zellner, R., "Recombination Reactions in Atmospheric Chemistry," *Ber. Bunsenges. Phys. Chem.* **82**, 1172-1179 (1978)
- P. F. Raspeon
June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Temp. Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncertainty Factor at 298K, notes |
|-------|---|------------------|--|--------------------------------------|
| | | | | |
| 19.32 | H ₂ + H ₂ S → H ₂ O + H ₂ | | ΔE (298) = -114 kJ/mol | |
| | NASA (1979) eval | 200-300 | 1.1 x 10 ⁻¹¹ exp(-(220±220)/T) | 1.25 |
| | CODATA (1979) eval | 250-400 | 1.4 x 10 ⁻¹¹ exp(-(225±225)/T) | 1.25 |
| | Baulch, et al (1976) review | 300-500 | 1.05 x 10 ⁻¹¹ exp(-200/T) | |
| | Perry, Atkinson, Pitts (1976a) | 297-427 | (5.2 ± 0.5) x 10 ⁻¹² | |
| | Stuhl (1974) | 298 | 3.1 ± 0.5 x 10 ⁻¹² | |
| | Westenberg, deHaas (1973) | 298-885 | 2.3 x 10 ⁻¹¹ exp(-440/T) | |

The recommended values for k (298 K) and E/E are the average of the values determined by Westenberg and deHaas (1973) and Perry et al (1976a). A log k has been chosen to encompass the value of Stuhl (1974) within the 2 σ error bands. A E/E was chosen to encompass both the 440 value of Westenberg and deHaas (1973) and the zero value of Perry et al (1976a). Although 2 x Δ E/E(2 σ) allows for a negative value, we do not expect E/E to be less than zero.

REFERENCES

- Baulch, D. L., Drysdale, D. D., Duxbury, J., and Grant, S. J., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 3: Homogeneous Gas Phase Reactions of the C₂-O₃ System, the C₆-O₂-H₂ System, and of Sulphur-Containing Species," (Butterworths, London, 1976)
- CODATA(1979). Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.
- NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," E. D. Hudson and E. L. Reed, Editors, Dec. 1979 (report of the June 1979 Harpers Ferry Workshop).

Perry, R. A., Atkinson, R., and Pitts, J. N., Jr., "Rate Constants for the Reactions $\text{OH} \cdot \text{H}_2\text{S} \rightarrow \text{H}_2\text{O} + \text{SH}$ and $\text{OH} \cdot \text{NH}_3 \rightarrow \text{H}_2\text{O} + \text{NH}_2$ over the Temperature Range 297-427°K.," *J. Chem. Phys.* **61**, 3237-3239 (1974a)

Stuhl, F., "Determination of the Rate Constant for the Reaction $\text{OH} \cdot \text{H}_2\text{S}$ by a Pulsed Photolysis - Resonance Fluorescence Method," *Rev. Phys. Chem.* **48**, 230-232 (1974)

Westenberg, A. A., and deHaas, M., "Rate of the Reaction $\text{OH} \cdot \text{H}_2\text{S} \rightarrow \text{SH} + \text{H}_2\text{O}$ over an Extended Temperature Range," *J. Chem. Phys.* **52**, 6685-6686 (1973)

R. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Temp. Range/K | Reaction Rate Constant $k/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$ | Uncertainty Factor at 258K, notes |
|--------|---|------------------|--|--------------------------------------|
| 19,34b | $\text{BC} + \text{CS}_2 \rightarrow \text{products}$ | | | |
| | NASA (1979) eval | 258 | 1.5×10^{-13} | 2 |
| | CODATA (1979) eval | 258 | 42×10^{-13} | 5 |
| | Kurylo (1978) | 256 | $(1.85 \pm 0.34) \times 10^{-13}$ | |
| | Atkinson, et al (1978) | 300 | 47×10^{-14} | |

The $k(298 \text{ K})$ value is that reported by Kurylo (1978). The observations in this study at higher reactant pressures (a nonlinear dependence of first-order OH decay rates on reactant concentration were similar to those of Atkinson et al (1978) who set an upper limit considerably below the value recommended here. Kurylo attributed these observations to complications associated with secondary reactions. Under more stringent experimental conditions (lower reactant concentration and lower free radical concentrations), well-behaved kinetic results were obtained. These latter results were interpreted as being free from secondary reaction complications. Further study is recommended to determine the validity of this interpretation. There are no measurements of the temperature dependence of this reaction. In the absence of any direct mechanistic information, no estimate of E^\ddagger or the A-factor can be given.

The uncertainty factor in $k(298 \text{ K})$ has been increased since the evaluation in Bowers et al (1979) to reflect the complexity of the kinetic analysis used to derive $k(258 \text{ K})$. This increase does not permit overlap of $k(298 \text{ K})$ from both literature studies. Further study is still needed to establish the validity of the interpretation upon which the present recommendation is based. Measurements at both the temperature dependence of k and the mechanism of the reaction are essential. If suggestions regarding a possible addition mechanism (Kurylo and Laufer (1975)) are correct, the reaction may have a negative temperature dependence.

REFERENCES

- Atkinson, B., Ferry, B. A., and Pitts, J. N. Jr., "Rate Constants for the Reaction of OH Radicals with CCl_4 , CS_2 and CH_3SCH_3 over the Temperature Range 299-430 K," *Chem. Phys. Lett.* **54**, 14-18 (1978)
- CODATA(1979). Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the *Journal of Physical and Chemical Reference Data*.

Demers, R. B., Stief, L. J., Kaufman, F., Golden, D. M., Hampson, R. F., Kurylo, M. J., Margitan, J. J., Molina, M. J., and Watson, M. T., "Chemical Kinetic and Photochemical Data for use in Stratospheric Modelling," JPL Publication 79-27, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California, 1979.

Kurylo, M. J., "Flash Photolysis Resonance Fluorescence Investigation of the Reactions of OH Radicals with OCS and CS₂," Chem. Phys. Lett. **58**, 238-242 (1978)

Kurylo, M. J., and Laufer, A. H., "Evidence for Atom Exchange in OH Reactions with Carbonyl Compounds: $18\text{OH} + \text{CO}_2 \rightarrow 18\text{OCCO} + \text{OH}$; $18\text{OH} + \text{C}_6\text{H}_6 \rightarrow 18\text{OC} + \text{OH}$," J. Chem. Phys. **70**, 2022-2033 (1979)

NASA (1979), Recommendations of the NASA Panel for Data Evaluation, published in NASA EP 1049 "The Stratosphere: Present and Future," R. D. Hudson and E. L. Reed, Editors, Dec. 1975 (report of the June 1975 Harpers Ferry Workshop).

R. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Uncert. Factor
at 298K, notes

2
5

| Mo. | Reaction/Reference | Temp. Range/K | Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$ |
|--------|---|------------------|---|
| 19.34c | NO + C ₂ H ₄ → Products | | |
| | NASA (1979) eval | 298 | 5.6×10^{-14} |
| | CODATA (1979) eval | 298 | 46×10^{-14} |
| | Eurylo (1978) | 256 | $(5.66 \pm 1.2) \times 10^{-14}$ |
| | Atkinson, et al (1978) | 299 | 47×10^{-15} |

The $k(298 K)$ value is that reported by Eurylo (1978). The observations in this study at higher reactant pressures (a nonlinear dependence of first-order OH decay rates on reactant concentration were similar to those of Atkinson et al (1978) who set an upper limit considerably below the value recommended here. Eurylo attributed these observations to complications associated with secondary reactions. Under more stringent experimental conditions (lower reactant concentration and lower free radical concentrations), well-behaved kinetic results were obtained. These latter results were interpreted as being free from secondary reaction complications. Further study is recommended to determine the validity of this interpretation. There are no measurements of the temperature dependence of this reaction. In the absence of any direct mechanistic information, no estimate of E/R or the A -factor can be given.

The uncertainty factor in $k(298 K)$ has been increased since the evaluation in DeMore et al (1979) to reflect the complexity of the kinetic analysis used to derive $k(298 K)$. This increase does not permit overlap of $k(298 K)$ from both literature studies. Further study is still needed to establish the validity of the interpretation upon which the present recommendation is based. Measurements at both the temperature dependence of k and the mechanism of the reaction are essential. If suggestions regarding a possible addition mechanism (Eurylo and Laufer (1975)) are correct, the reaction may have a negative temperature dependence.

REFERENCES

- Atkinson, R., Perry, R. A., and Pitts, J. N. Jr., "Rate Constants for the Reaction of OH Radicals with C₂H₄, C₂H₆ and CH₃CH₃ over the Temperature Range 299-430 K," *Chem. Phys. Lett.* **54**, 14-16 (1978)
- CODATA(1979), Recommendations of the CODATA Task Group on Chemical Kinetics, To be published in the Journal of Physical and Chemical Reference Data.

DeMore, W. B., Stief, L. J., Kaufman, F., Golden, D. M., Hampson, R. F., Kurylo, M. J., Mergitan, J. J., Molina, M. J., and Watson, R. T., "Chemical Kinetic and Photochemical Data for use in Stratospheric Modelling," JPL Publication 79-27, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California, 1979.

Kurylo, M. J., "Flash Photolysis Resonance Fluorescence Investigation of the Reactions of CH Radicals with OCS and CH_2 ," *Chem. Phys. Lett.* **58**, 238-242 (1978)

Kurylo, M. J., and Laufer, A. E., "Evidence for Atom Exchange in CH Reactions with Carbonyl Compounds: $18\text{OH} + \text{CO}_2 \rightarrow 18\text{CO} + \text{OH}$; $18\text{H} + \text{CC} \rightarrow 18\text{C} + \text{CH}$," *J. Chem. Phys.* **70**, 2032-2033 (1979)

NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," E. D. Hudson and E. L. Reed, Editors, Dec. 1975 (report of the June 1975 Barbers Ferry Workshop).

R. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Uncertainty Factor
 at 250K, notes

| No. | Reaction/Reference | Temp. Range/K | Reaction Rate Constant $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | Uncertainty Factor at 250K, notes |
|-------|---|------------------|--|--------------------------------------|
| 19,36 | $\text{H}_2 + \text{ClO} \rightarrow \text{products}$ | | | |
| | NASA (1979) eval | 250 | 5.1×10^{-12} | 1.4 |
| | CODATA (1975) eval | 250 | 5.1×10^{-12} | 2 |
| | Lou, Lin (1976) | 250 | $(9.1 \pm 1.3) \times 10^{-12}$ | |

Value reported by Lou and Lin (1976). A lower limit of 0.65 was determined for $k_1(\text{CH} + \text{ClO} \rightarrow \text{H}_2 + \text{Cl})/k_1(\text{CH} + \text{ClO} \rightarrow \text{products})$ at 250K. The actual value of k_1/k_2 may possibly be unity

REFERENCES

- CODATA(1979). Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.
- Lou, M. T., and Lin, C. L., "Rate Constants for the Reactions of CH with ClO, Cl₂, and Cl₂O at 250K," *Geophysics Res. Lett.* **6**, 425-428 (1979)
- NASA (1979). Recommendations of the NASA Panel for Data Evaluation. published in NASA SP 1049 "The Stratosphere: Present and Future."
- M. R. Hudson and E. I. Reed, Editors, Dec. 1976 (report of the June 1976 Harpers Ferry Workshop).
- M. R. Hampson
 June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Temp. Range/K | Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$ | Uncertainty Factor at 298K, notes |
|---------|---|------------------|---|--------------------------------------|
| 19,368r | $H_2 + Br_2 \rightarrow products$ NASA (1979) eval | 298 | 5×10^{-12} | 5 |

No data; value chosen to be consistent with $k(H_2 + Cl_2)$

REFERENCES

NASA (1979). Recommendations of the NASA Panel for Data Evaluation.
published in NASA SP 1049 "The Stratosphere: Present and Future,"
B. D. Hudson and E. L. Reed, Editors, Dec. 1975 (report of the
June 1975 Harpers Ferry Workshop).

E. P. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Uncertainty Factor
 at 298K, notes

Reaction Rate Constant
 $k/cm^3 molecule^{-1} s^{-1}$

Temp.
 Range/K

Reaction/Reference

No.

| | | | | |
|-------|-----------------------------------|---------|--|-------|
| 19,39 | $H_2 + HCl \rightarrow H_2O + Cl$ | | $\Delta H (298) = -67 \text{ kJ/mol}$ | |
| | NASA (1979) eval | 200-300 | $2.8 \times 10^{-12} \exp(-(425 \pm 100)/T)$ | 1.015 |
| | CCDATA (1979) eval | 210-460 | $3.0 \times 10^{-12} \exp(-(425 \pm 100)/T)$ | 1.015 |
| | Watson (1977) review | 220-300 | $3.0 \times 10^{-12} \exp(-425/T)$ | |
| | Smith, Zellner (1974a) | 210-460 | $4.1 \times 10^{-12} \exp(-530/T)$ | |
| | Zahniser, et al (1974) | 224-460 | $2.0 \times 10^{-12} \exp(-312/T)$ | |
| | Ravishankara, et al (1977) | 250-402 | $3.3 \times 10^{-12} \exp(-472/T)$ | |
| | Hack, Mex, Wagner (1977) | 293 | 6.6×10^{-13} | |
| | Takacs, Glass (1973b) | 295 | $6.4 \pm 1.5 \times 10^{-13}$ | |

Unchanged from NASA 1010. There is good agreement between all groups of workers at ~ 298 K (Takacs and Glass (1973b); Zahniser et al (1974), Smith and Zellner (1974), Ravishankara et al (1977a), and Hack et al (1977a) and the preferred value at this temperature is the average. The Arrhenius expression was derived by giving an equal weighting to data reported by Zahniser et al, Ravishankara et al and Smith and Zellner

REFERENCES

CCDATA(1979). Recommendations of the CCData Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.

Hack, W., Mex, G., and Wagner, H. G., "Bestimmung der Geschwindigkeitskonstanten der Reaktionen $H + HCl$ im Temperaturbereich 293 bis 718 K und $OH + HCl$ bei 293 K," Ber. Bunsenges. Phys. Chem. **81**, 677-684 (1977)

NASA RP-1010. "Chlorofluoromethanes and the Stratosphere" R. D. Hudson, Editor, August 1977 This reference contains the NASA (1977) rate constant recommendations.
 NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," R. D. Hudson and E. L. Reed, Editors, Dec. 1979 (report of the June 1979 Harpers Ferry Workshop).

- Davieshankar, A. R., Smith, G., Watson, R. T., and Davis, D. D.,
"A Temperature Dependent Kinetics Study of the Reactions
of HCl with OH and O(3P)," *J. Phys. Chem.* **81**, 2220-2225
(1977a)
- Smith, I. W. M., and Zellner, R., "Rate Measurements of Reactions of OH
by Resonance Absorption. Part 3. Reactions of CH with H₂, D₂, Hydrogen
and Deuterium Halides," *J. Chem. Soc., Faraday Trans. II* **70**, 1045-1056 (1974a)
- Telieps, G. A., and Glass, G. P., "Reactions of Hydroxyl Radicals with Some
Hydrogen Halides," *J. Phys. Chem.* **77**, 1948-1951 (1973)
- Watson, R. T., "Rate Constants for Reactions of ClO₂ of Atmospheric
Interest," *J. Phys. Chem. Ref. Data* **6**, 871-918 (1977)
- Zehner, M. G., Kaufman, F., and Anderson, J. G., "Kinetics of the Reaction
of OH with HCl," *Chem. Phys. Lett.* **27**, 507-510 (1974)
- R. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY
 PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Reaction/Reference
 Tempo
 Range/K
 Reaction Rate Constant
 $\text{k/cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
 Uncert. Factor
 at 298K, notes

| No. | Reaction/Reference | Tempo Range/K | Reaction Rate Constant $\text{k/cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | Uncert. Factor at 298K, notes |
|--------|---|------------------|--|----------------------------------|
| 19,39D | $\text{Hd} + \text{DCI} \rightarrow \text{HDd} + \text{Cl}$ Smith, Zellner (1974a) | 210-460 | $4.7 \times 10^{-12} \exp(-780/T)$ | |

Only reported value - no recommendation

REFERENCES

Smith, I. W. M., and Zellner, R., "Rate Measurements of Reactions of CH
 by Resonance Absorption. Part 3. Reactions of CH with H₂, D₂, Hydrogen
 and Deuterium Halides," J. Chem. Soc., Faraday Trans. II **70**, 1045-1056 (1974a)

R. F. Hampson
 May 1978

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CBER

 $\text{m}^3/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ No.

Changed from NASA 1010 due to new data. Takeace and Glass (1973a) combined their results with those of

REFERENCES

CDATA(1979). Recommendations of the CDATA Task Group on Chemical

NASA RP-1010. "Chlorofluoromethanes and the Stratosphere"

Dr. Hudson. Editor. August 1977 This reference contains

the NASA (1977) rate constant recommendations.

NASA (1979). Recommendations of the NASA Panel for Data Evaluation,

published in NASA RP 1049 "The Stratosphere: Present and Future,"

R. D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the

June 1979 Harper Ferry Workshop).

Devishankar, A. K., Mino, P. K., and Langford, A. G., "Absolute Rate Constant for the Reaction $\text{OH} + \text{HBr} \rightarrow \text{H}_2\text{O} + \text{Br}$," *Chem. Phys. Lett.* **53**, 479-484 (1979)

Tokacs, G. A., and Glass, G. P., "Reactions of Hydrogen Atoms and Hydroxyl Radicals with Hydrogen Bromide," *J. Phys. Chem.* **77**, 1060-1064 (1973a)
Wilson, W. K., Jr., O'Donovan, J. T., and Fristrom, R. M., "Flame Inhibition by Halogen Compounds," *Symp. Combust.* **12**, (Combustion Institute, Pittsburgh, Pa., 1969) 529-942

P. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Temp. Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncert. Factor at 298K, notes |
|-------|--|------------------|--|----------------------------------|
| 19.40 | H ₂ + HgCl → H ₂ + Cl ₂ NASA (1979) eval | 200-300 | $\Delta H(298) = -101 \text{ kJ/mol}$ $3 \times 10^{-12} \exp(-(200+500)/T)$ | 10 |

New entry. There are no experimental data for this reaction. This is an estimated value based on observed rates of OH reaction with similar compounds, combined with an estimated A-factor

REFERENCES

NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA SP 1049 "The Stratosphere: Present and Future,"
R. D. Hudson and E. L. Reed, Editors, Dec. 1975 (report of the
June 1975 Harpers Ferry Workshop).

R. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Uncertain Factor
at 298K, notes

Reaction/Reference

Tempo
Range/K

Reaction Rate Constant
k/cm³molecule⁻¹s⁻¹

No.

| | | | | | |
|--------|--|---------|---|--|-----|
| 19.43a | H ₂ + NO ₂ Cl → products | | | | 1.5 |
| | NASA (1979) eval | 200-300 | $1.2 \times 10^{-12} \exp(-333 \pm 200)/T)$ | | 1.5 |
| | CODATA (1979) eval | 246-387 | $1.2 \times 10^{-12} \exp(-330 \pm 200)/T)$ | | |
| | Zahniser, et al (1977) | 246-387 | $(1.19 \pm 0.10) \times 10^{-12} \exp(-333 \pm 22/T)$ | | |
| | Pavlishankara, et al (1977) | 245 | 3.7×10^{-13} | | |

Unchanged from NASA 1010. The results reported by Zahniser et al (1977) and Pavlishankara et al (1977) are in good agreement at ~ 245 K (within 25%) considering the difficulties associated with handling ClONO₂. The preferred value is that of Zahniser et al. Neither study reported any data on the reaction products

REFERENCES

CODATA (1979). Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.

NASA RP-1010. "Chlorofluoromethanes and the Stratosphere"

R. D. Hudson, Editor, August 1977 This reference contains the NASA (1977) rate constant recommendations.

NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," R. D. Hudson and E. L. Reed, Editors, Dec. 1979 (report of the June 1979 Harpers Ferry Workshop).

Pavlishankara, A. R. Davis, D. D. Smith, G. Tosi, G., and Spencer, J., "A Study of the Chemical Degradation of ClONO₂ in the Stratosphere," Geophys. Res. Lett. **4**, 7-9 (1977)

Zahniser, M. S., Chang, J. S., and Kaufman, F., "Chlorine Nitrate: Kinetics of Formation by ClO + NO₂ + M and of Reaction with OH," J. Chem. Phys. **67**, 997-1003 (1977)

R. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY

Reaction Rate Constant
 $k/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$

Reaction Rate Constant
 $k/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$

| Ref | Reaction | Temp (K) | Pressure (atm) | Notes |
|-----------------------------------|-------------------------------------|----------|----------------|-------|
| 19,45 | $H_2 + CO \rightarrow CH_4 + H$ (f) | | | |
| 19,46 | $H + CO_2 \rightarrow H_2 + CO$ (r) | | | |
| NASA (1979) | eval | | | |
| CeDATA (1979) | eval | | | |
| Baulch, et al (1976) | review | | | |
| 200-300 | | | | |
| 200-300 | | | | |
| 296 | | | | |
| 250-2500 | | | | |
| 1000-3000 | | | | |
| 300 | | | | |
| Biermann, et al (1978) | | | | |
| 298 | | | | |
| Butler, et al (1978) | | | | |
| 298 | | | | |
| Chan, et al (1977) | | | | |
| 298 | | | | |
| Sie, Simonaitis, Reichlen (1976a) | | | | |
| 217-298 | | | | |
| 298 | | | | |
| 296 | | | | |
| Cox, Derwent, Holt (1976) | | | | |
| 299 | | | | |
| Aspinos, Perry, Pitts (1976a) | | | | |

| Perry, Atkinson, Pitts (1977a) | 259 | $10^{13} \frac{A}{k}$ | $E(\text{SE}_6)/\text{torr}$ |
|--|-----------|---|--|
| | | 1.53 | 25 |
| | | 1.93 | 76 |
| | | 2.40 | 208 |
| | | 2.09 | 403 |
| | | 2.43 | 603 |
| Overend, Paraskevopoulos (1977) | 256 | $(2.03 \pm 0.08) \times 10^{-13}$ | at 50 torr He |
| Gordon, Mular (1975) | 298 | $(3.24 \pm 0.20) \times 10^{-13}$ | at 200, 350 torr SF_6 |
| | | 1.50×10^{-13} | at 710 torr Ar, 10 torr H_2O |
| <u>Experiments either at low pressures or for which pressure effects have not studied.</u> | | | |
| Trainer, von Rosenberg (1975) | 300 | 1.25×10^{-13} | |
| Vandeoren, et al (1975) | 400-800 | 1.33×10^{-13} | |
| | 1000-1800 | 3.25×10^{-12} | $\exp(-2850/T)$ |
| Bjordi, et al (1975) | 1350-1750 | 7.6×10^{-13} | |
| Steinert, Zellner (1975) | 300-900 | $\log k = -12.93 + 4.0 \times 10^{-4} \times T$ | |
| Wilson (1972) review | 300-2000 | 5.1×10^{-13} | $\exp(-300/T)$ |
| Stuhl, Niki (1972) | 300 | 1.25×10^{-13} | |
| Westenberg, deHaas (1973a) | 298-915 | $k(298) = 1.33 \times 10^{-13}$ | |
| Davis, Fischer, Schiff (1974) | 220-373 | $2.15 \pm 0.19 \times 10^{-13}$ | $\exp(-80 \pm 40/T)$ |
| Greiner (1969) | 300-500 | 2.1×10^{-13} | $\exp(-115/T)$ |
| Smith, Zellner (1973) | 300 | 1.45×10^{-13} | |
| | | Data reported 210 < T < 460 K. Slight positive temperature dependence, possibly curved. | |
| Peeters, Mahnen (1973) | 1600-1900 | 4.7×10^{-13} | |
| Gardiner, et al (1973) | 1500-2000 | 6.7×10^{-12} | $\exp(-4000/T)$ |
| Roward, Evenson (1974) | 256 | $1.56 \pm 0.2 \times 10^{-13}$ | |

The recommended expression allows for the factor of 2 increase in k seen in several studies at 1 atm pressures of non-inert gases. The most detailed study (Biermann et al (1978)) found that the pressure effect requires either (a) small amounts of O_2 (> 0.25 torr) or (b) the presence of other impurities. Further study of the combined pressure and temperature effects is needed.

REFERENCES

- Atkinson, P., Perry, P. A., and Pitts, J. N., Jr., "Kinetics of the Reactions of OH Radicals with CO and N_2O ," *Chem. Phys. Lett.* **44**, 204-208 (1976a)
- Baulch, D. L., Drysdale, D. D., Duxbury, J., and Grant, S. J., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 3: Homogeneous Gas Phase Reactions of the O_2 - O_3 System, the CO - O_2 - H_2 System, and of Sulphur-Containing Species," (Butterworths, London, 1976)
- Biermann, H. W., Zetzsch, C., and Stuhl, F., "On the Pressure Dependence of the Reaction of HO with CO ," *Ber. Bunsenges. Phys. Chem.* **82**, 633-639 (1978)

- Bierdi, J. C., Lazzard, C. P., and Papp, J. E., "Flame Structure Studies of C_2H_2 -Inhibited Methane Flames. II. Kinetics and Mechanisms," Symp. Combust. 15th (Combustion Institute, Pittsburgh, 1975) 917-932
- Butler, R., Solomon, I. J., and Snellson, A., "Pressure Dependence of the $\text{CO} + \text{OH}$ Rate Constant in $\text{O}_2 + \text{N}_2$ Mixtures," Chem. Phys. Lett. 51, 19-24 (1978)
- Chan, W. M., Uselman, W. M., Calvert, J. G., and Shaw, J. H., "The Pressure Dependence of the Rate Constant for the Reaction: $\text{NO} + \text{CO} \rightarrow \text{N} + \text{CO}_2$," Chem. Phys. Lett. 45, 240-244 (1977)
- CODATA(1979). Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.
- Cox, R. A., Derwent, R. G., and Holt, P. M., "Relative Rate Constants for the Reactions of OH Radicals with H_2 , CH_4 , C_2H_6 , C_3H_8 and HCHO at Atmospheric Pressure and 296 K," J. Chem. Soc., Faraday Trans. 1 72, 2031-2043 (1976)
- Davis, D. D., Fischer, S., and Schiff, R., "Flash Photolysis-Resonance Fluorescence Kinetics Study: Temperature Dependence of the Reactions $\text{OH} + \text{CO} \rightarrow \text{CO}_2 + \text{H}$ and $\text{OH} + \text{CH}_4 \rightarrow \text{H}_2\text{O} + \text{CH}_3$," J. Chem. Phys. 61, 2213-2219 (1974)
- Gardiner, W. C., Jr., Mallard, W. G., McFarland, M., Morinaga, L., Gven, J. E., Ravlin, W. J., Takeyama, T., and Walker, R. E., "Elementary Reaction Rates from Post-Induction-Period Profiles in Shock-Initiated Combustion," Symp. Combust. 14th (Combustion Institute, Pittsburgh, 1973) 61-72
- Gordon, S., and Mulaic, R. A., "Reaction of the $\text{OH}(\text{X}^2\text{P})$ Radical Produced by the Pulse Radiolysis of Water Vapor," Int. J. Chem. Kinet., Symp. No. 1, 289-299 (1975)
- Greiner, M. P., "Hydroxyl Radical Kinetics by Kinetic Spectroscopy. V. Reactions with H_2 and CO in the Range 300-500°K," J. Chem. Phys. 51, 5049-5051 (1969)
- Howard, C. J., and Evenson, L. M., "Laser Magnetic Resonance Study of the Gas Phase Reactions of OH with CO , NO , and NO_2 ," J. Chem. Phys. 51, 1943-1952 (1974)
- NAEA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," R. D. Hudson and E. L. Reed, Editors, Dec. 1975 (report of the June 1979 Harpers Ferry Workshop).
- Overend, R., and Paraskevopoulos, G., "The Question of a Pressure Effect in the Reaction $\text{OH} + \text{CO}$ at Room Temperature," Chem. Phys. Lett. 49, 109-111 (1977)

- Peeters, Jo. and Mahnen, G., "Reaction Mechanisms and Rate Constants of Elementary Steps in Methane-Oxygen Flames," Symp. Combust. 14th (Combustion Institute, Pittsburgh, 1973) 133-141
- Perry, P. A., Atkinson, P., and Pitts, J. N., Jr., "Kinetics of the Reactions of OH Radicals with C_2H_2 and CH_4 ," J. Chem. Phys. **67**, 5577-5584 (1977a)
- Sie, B. K. T., Simenault, R., and Reichlen, J., "The Reaction of OH with CO ," Int. J. Chem. Kinet. **2**, 85-98 (1976a)
- Smith, I. W. M., and Zellner, R., "Rate Measurements of Reactions of OH by Resonance Absorption Part 2. Reactions of OH with CO , C_2H_4 , and C_2H_2 ," J. Chem. Soc., Faraday Trans. II **69**, 1617-1627 (1973)
- Steinert, W., and Zellner, R., "Rates of Reaction of OH with CO and CH_4 over an Extended Temperature Range," Deuxieme Symp. European sur la Combustion (Orleans, 1975) 31-37
- Stuhl, F., and Miki, W., "Pulsed Vacuum-uv Photochemical Study of Reactions of OH with H_2 , D_2 , and CH_4 Using a Resonance-Fluorescent Detection Method," J. Chem. Phys. **57**, 3671-3677 (1972)
- Trainer, D. W., and von Rosenberg, C. W., Jr., "Energy Partitioning in the Products of Elementary Reactions Involving OH-Radicals," Symp. Combust. 15th (Combustion Institute, Pittsburgh, 1975) 755-764
- Vandoren, J., Peeters, J., and Van Hisselen, P. J., "Rate Constant of the Elementary Reaction of Carbon Monoxide with Hydroxyl Radical," Symp. Combust. 15th (Combustion Institute, Pittsburgh, 1975) 745-752
- Westenberg, A. A., and deHaas, N., "Rates of $CO + OH$ and $H_2 + OH$ over an Extended Temperature Range," J. Chem. Phys. **58**, 4061-4065 (1973a)
- Wilson, W. E., Jr., "A Critical Review of the Gas-Phase Reaction Kinetics of the Hydroxyl Radical," J. Phys. Chem. Ref. Data **1**, 535-573 (1972)

W. F. Hanson
June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Uncert. Factor
at 298K, notes

Reaction Rate Constant
k/cm³ molecule⁻¹ s⁻¹

Tempo
Range/K

Reaction/Reference

No.

| | | | | |
|-------|---|---|---------|-------|
| 19.48 | H ₂ + CH ₂ = H ₂ C + CH ₂ | ΔH (292) = -135 kJ/mol | | |
| | NASA (1979) eval | 1.0 x 10 ⁻¹¹ exp((0±200)/T) | 200-300 | 1.025 |
| | CODATA (1979) eval | 1.3 x 10 ⁻¹¹ exp((0±200)/T) | 200-400 | 1.04 |
| | Atkinson, Pitts (1978) | 1.25 x 10 ⁻¹¹ exp(-(90±150)/T) | 259-426 | |
| | Stief, et al (1979) | (1.05±0.22) x 10 ⁻¹¹ | 228-362 | |
| | Morris, Niki (1971) | (1.4±0.3) x 10 ⁻¹¹ | 300 | |
| | Niki, et al (1978) | (1.5±0.1) x 10 ⁻¹¹ | 298 | |
| | Smith (1978) | (6.5±1.5) x 10 ⁻¹² | 298 | |

The value for k(298) is the average of those determined by Atkinson and Pitts (1978) and Stief et al (1979), both using the flash photolysis - resonance fluorescence technique. The value reported by Morris and Niki (1971) agrees within the stated uncertainty. There are two relative values which are not in agreement with the recommendations. The value of Niki et al (1978) relative to OH + C₂H₄ is higher while the value of Smith (1978) relative to OH + OH is lower. The latter data is also at variance with the negligible temperature dependence observed in the two flash photolysis studies. Although Atkinson and Pitts assign a small energy barrier (E/R = 90 ± 150), their data at 356K and 426K and that of Stief et al at 228K, 257K and 362K are all within 10% of the k(298) value. Thus the combined data set suggest E/R = 0.

The abstraction reaction given is probably the major channel; other channels may contribute (Korowitz et al 1978).

REFERENCES

- Atkinson, P., and Pitts, J. N. Jr., "Kinetics of the Reactions of the OH Radical with HCHO and CH₃CHO over the Temperature Range 299-426°K," *J. Chem. Phys.* **58**, 3561-3564 (1978)
- CODATA(1979). Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the *Journal of Physical and Chemical Reference Data*
- Korowitz, A., Su, F., and Calvert, J. G., "Unusual H₂-Forming Chain Reaction in the 3130-Å Photolysis of Formaldehyde-Oxygen Mixtures at 25°C," *Int. J. Chem. Kinet.* **10**, 1099-1117 (1978)
- Morris, E. B., Jr., and Niki, H., "Mass Spectrometric Study of the Reaction of Hydroxyl Radical with Formaldehyde," *J. Chem. Phys.* **55**, 1991-1992 (1971)

NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: present and Future." P. D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the June 1975 Harpers Ferry Workshop).

Viki, R. O., Maher, P. D., Savage, C. M., and Breitenbach, L. P., "Relative Rate Constants for the Reaction of Hydroxyl Radical with Aldehydes," *J. Phys. Chem.* **82**, 132-134 (1978)

With, R. O., "Rate Constant and Activation Energy for the Gaseous Reaction Between Hydroxyl and Formaldehyde," *Int. J. Chem. Kinet.* **10**, 519-528 (1978)

Wief, T. J., Nava, D. R., Payne, W. A., and Michael, J. V., manuscript in preparation, 1979.

W. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Uncertainty Factor
at 298K, notes

Reaction Rate Constant
 $k/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$

Tempo
Range/K

No.

| | | | |
|-------|---|-----|------------------------|
| 14,52 | $\text{H}_2 + \text{CH}_3\text{OH} \rightarrow \text{products}$ | | |
| | Everend, Paraskevopoulos (1978) | 296 | 1.06×10^{-12} |
| | Campbell, et al (1976) | 292 | 9.5×10^{-13} |

No recommendation

REFERENCES

Campbell, I. M., McLaughlin, D. F., and Handy, B. J., "Rate Constants for Reactions of Hydroxyl Radicals with Alcohol Vapours at 292 K," *Chem. Phys. Lett.* **38**, 362-364 (1976)

Everend, R., and Paraskevopoulos, G., "Rates of OH Radical Reactions with Methanol, Ethanol, 1-Propanol, and 2-Propanol at 296 K," *J. Phys. Chem.* **82**, 1325-1333 (1978)

P. F. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Temp. Range/K | Reaction Rate Constant $k/\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ | Uncert. Factor at 298K, notes |
|-------|---|------------------|--|----------------------------------|
| 19.53 | $\text{H} + \text{CH}_3\text{OH} \rightarrow \text{products}$ NASA (1979) eval | 200-300 | $1 \times 10^{-11} \exp(-7500/250/T)$ | 5 |

This estimate is based on an assumed similarity to $\text{OH} + \text{H}_2\text{O}_2$ and $\text{OH} + \text{CH}_3\text{OH}$. The $k(298)$ values for these two reactions are reported to be very similar:

$k(\text{OH} + \text{H}_2\text{O}_2) = 8.1 \times 10^{-13} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ (this evaluation) and

$k(\text{OH} + \text{CH}_3\text{OH}) = 9.5 \times 10^{-13} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ (Campbell et al. 1976).

In the absence of temperature dependent data for $\text{OH} + \text{CH}_3\text{OH}$, the A-factor and E/B values are assumed to be the same as those for $\text{OH} + \text{H}_2\text{O}_2$. The latter values are somewhat uncertain at present. The reaction products are not specified since, using the above analogies to CH_3OH and H_2O_2 , abstraction of H from either end of the molecules may be equally probable.

REFERENCES

Campbell, I. M., McLaughlin, D. F., and Handy, B. J., "Rate Constants for Reactions of Hydroxyl Radicals with Alcohol Vapors at 292 K," *Chem. Phys. Lett.* **35**, 362-364 (1976)

NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA BP 1049 "The Stratosphere: Present and Future," B. D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the June 1975 Harpers Ferry Workshop).

B. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Uncertainty Factor
at 298K, notes

| No. | Reaction/Reference | Temp. Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ |
|-------|--|------------------|--|
| 19,54 | NO + CH ₃ NO ₂ → products Campbell, Goodson (1975b) | 292 | 9.2 × 10 ⁻¹³ |

No recommendation

REFERENCES

Campbell, I. M., and Goodson, K. "Rate Constants for Reactions of Hydroxyl Radicals with Nitromethane and Methyl Nitrite Vapours at 292 K," *Chem. Phys. Lett.* **36**, 382-384 (1975b)

R. F. Hampson
May 1976

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Uncert. Factor
at 298K, notes

Reaction/Reference Temp.
Range/K k/cm³molecule⁻¹s⁻¹

No.

| | | | |
|-------|------------------------------------|-----|-------------------------|
| 19,54 | 20 + CH ₃ OH → products | 292 | 1.3 × 10 ⁻¹² |
| | Campbell, Goodman (1975b) | | |

No recommendation

REFERENCES

Campbell, I. M., and Goodman, K., "Rate Constants for Reactions of Hydroxyl Radicals with Nitromethane and Methyl Nitrite Vapours at 292 K," *Chem. Phys. Lett.* **36**, 382-384 (1975b)

E. F. Hansen
May 1978

CHEMICAL KINETICS DATA SURVEY
 PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Reaction/Reference
 Temp.
 Range/K
 Reaction Rate Constant
 $k/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$
 Uncert. Factor
 at 298K, notes

| No. | Reaction/Reference | Temp. Range/K | Reaction Rate Constant $k/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$ | Uncert. Factor at 298K, notes |
|-------|---|------------------|---|----------------------------------|
| 19,56 | $\text{H}^\bullet + \text{CH}_4 \rightarrow \text{CH}_3 + \text{H}_2^\bullet$ | | $\Delta H (298) = -60 \text{ kJ/mol}$ | |
| | NASA (1979) eval | 280-300 | $2.4 \times 10^{-12} \exp(-1710/200/T)$ | 1.2 |
| | CcDATA (1979) eval | 200-300 | $2.4 \times 10^{-12} \exp(-1710/200/T)$ | 1.25 |
| | Davis, Fischer, Schiff (1974) | 240-373 | $2.36 \pm 0.21 \times 10^{-12} \exp(-1710 \pm 88/T)$ | |
| | Margitan, et al (1974) | 290-440 | $3.83 \times 10^{-12} \exp(-1840 \pm 20/T)$ | |
| | Zellner, Steinert (1976) | 300-900 | $5.76 \times 10^{-12} \exp(-1010/T)$ | |
| | Greiner (1970) | 300-500 | $5.5 \times 10^{-12} \exp(-1900/T)$ | |
| | Overend, et al (1975) | 300 | $6.51 \pm 0.26 \times 10^{-15}$ | |
| | Peeters, Mahnen (1973) | 1100-1900 | $5 \times 10^{-11} \exp(-3000/T)$ | |
| | Gordon, Mulae (1975) | 381 | $2.6 \times 10^{-14} \quad (1 \text{ atm } \text{H}_2^\bullet \text{ vapor})$ | |
| | | 416 | $5.5 \times 10^{-14} \quad (1 \text{ atm } \text{H}_2^\bullet \text{ vapor})$ | |
| | Howard, Evenson (1976a) | 296 | $(9.5 \pm 1.4) \times 10^{-15}$ | |
| | Cox, Derwent, Holt (1976) | 296 | $(7.3 \pm 0.9) \times 10^{-15}$ | |
| | | | ref rxn is $\text{H}^\bullet + \text{H}_2 \rightarrow \text{H}_2^\bullet + \text{H}$ with $k_{\text{ref}} = 7 \times 10^{-15}$ | |

This reaction is one of the few not requiring further work. All four T dependence studies are in excellent agreement. The recommendation is unchanged from other evaluations (NBS SP 513, NASA RP-1010)

REFERENCES

- CcDATA(1979). Recommendations of the CcDATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.
- Cox, R. A., Derwent, F. G., and Holt, F. M. "Relative Rate Constants for the Reactions of OH Radicals with H_2 , CH_4 , C_2H_6 , C_3H_8 and H_2O at Atmospheric Pressure and 296 K," J. Chem. Soc., Faraday Trans. 1 **72**, 2031-2042 (1976)

- Devia, D. De, Fischer, S., and Schlif, R., "Flash Photolysis-Resonance Fluorescence Kinetics Study: Temperature Dependence of the Reactions $\text{OH} + \text{C}_2\text{H}_2 \rightarrow \text{C}_2\text{H}_4 + \text{H}$ and $\text{OH} + \text{CH}_4 \rightarrow \text{H}_2\text{O} + \text{CH}_3$," *J. Chem. Phys.* **61**, 2213-2219 (1974)
- Gorden, S., and Muiac, W. A., "Reaction of the $\text{OH}(\text{X}^2\text{P})$ Radical Produced by the Pulse Radiolysis of Water Vapor," *Int. J. Chem. Kinet.*, Symp. No. 1, 289-295 (1975)
- Greiner, M. R., "Hydroxyl Radical Kinetics by Kinetic Spectroscopy. VI. Reactions with Alkanes in the Range 300-500°K," *J. Chem. Phys.* **53**, 1070-1076 (1970)
- Harrison, R. F., and Garvin, D., "Reaction Rate and Photochemical Data for Atmospheric Chemistry-1977" U.S. National Bureau of Standards Special Publication 513, May 1978.
- Howard, C. J., and Evenson, L. M., "Rate Constants for the Reactions OH with CH_4 and Fluorine, Chlorine, and Bromine Substituted Methanes at 296 K," *J. Chem. Phys.* **64**, 187-202 (1976a)
- Margitan, J. J., Kaufman, F., and Anderson, J. G., "The Reaction of OH with CH_4 ," *Geophys. Res. Lett.* **1**, 80-81 (1974)
- NASA RP-1010, "Chlorofluoromethanes and the Stratosphere" by D. Hudson, Editor, August 1977 This reference contains the NASA (1977) rate constant recommendations.
- NASA (1979), Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," by D. Hudson and E. L. Reed, Editors, Dec. 1979 (report of the June 1975 Harpers Ferry Workshop).
- Overend, P., Paraskevopoulos, G., and Cvitanovic, P. J., "Rates of OH Radical Reactions. I. Reactions with H_2 , CH_4 , C_2H_6 , and C_3H_8 at 295 K," *Can. J. Chem.* **53**, 3374-3382 (1975)
- Peeters, J., and Mahnen, G., "Reaction Mechanisms and Rate Constants of Elementary Steps in Methane-Oxygen Flames," *Symp. Combust.* 14th (Combustion Institute, Pittsburgh, 1973) 133-141
- Zellner, R., and Steinert, W., "Flash Photolysis Study of the Rate of the Reaction $\text{OH} + \text{CH}_4 \rightarrow \text{CH}_3 + \text{H}_2\text{O}$ over an Extended Temperature Range," *Int. J. Chem. Kinet.* **8**, 397-409 (1976)
- R. F. Harrison
June 1979

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| | Reaction/Reference | Tempo | Reaction Rate Constant |
|-----|--------------------|-------|------------------------|
| 1 | | | |
| 2 | | | |
| 3 | | | |
| 4 | | | |
| 5 | | | |
| 6 | | | |
| 7 | | | |
| 8 | | | |
| 9 | | | |
| 10 | | | |
| 11 | | | |
| 12 | | | |
| 13 | | | |
| 14 | | | |
| 15 | | | |
| 16 | | | |
| 17 | | | |
| 18 | | | |
| 19 | | | |
| 20 | | | |
| 21 | | | |
| 22 | | | |
| 23 | | | |
| 24 | | | |
| 25 | | | |
| 26 | | | |
| 27 | | | |
| 28 | | | |
| 29 | | | |
| 30 | | | |
| 31 | | | |
| 32 | | | |
| 33 | | | |
| 34 | | | |
| 35 | | | |
| 36 | | | |
| 37 | | | |
| 38 | | | |
| 39 | | | |
| 40 | | | |
| 41 | | | |
| 42 | | | |
| 43 | | | |
| 44 | | | |
| 45 | | | |
| 46 | | | |
| 47 | | | |
| 48 | | | |
| 49 | | | |
| 50 | | | |
| 51 | | | |
| 52 | | | |
| 53 | | | |
| 54 | | | |
| 55 | | | |
| 56 | | | |
| 57 | | | |
| 58 | | | |
| 59 | | | |
| 60 | | | |
| 61 | | | |
| 62 | | | |
| 63 | | | |
| 64 | | | |
| 65 | | | |
| 66 | | | |
| 67 | | | |
| 68 | | | |
| 69 | | | |
| 70 | | | |
| 71 | | | |
| 72 | | | |
| 73 | | | |
| 74 | | | |
| 75 | | | |
| 76 | | | |
| 77 | | | |
| 78 | | | |
| 79 | | | |
| 80 | | | |
| 81 | | | |
| 82 | | | |
| 83 | | | |
| 84 | | | |
| 85 | | | |
| 86 | | | |
| 87 | | | |
| 88 | | | |
| 89 | | | |
| 90 | | | |
| 91 | | | |
| 92 | | | |
| 93 | | | |
| 94 | | | |
| 95 | | | |
| 96 | | | |
| 97 | | | |
| 98 | | | |
| 99 | | | |
| 100 | | | |

Uncertainty Factor
at 298K, notes

| No. | Reaction/Reference | Tempo Range/K | Reaction Rate Constant $\text{l./cm}^3\text{-molecule}^{-1}\text{s}^{-1}$ | Uncertainty factor at 298K, notes |
|--------|---|------------------|--|---|
| 19,56a | $\text{H}_2 + \text{C}_2\text{H}_2 \rightarrow \text{products}$ | | | |
| | Smith, Zellner (1973) | 210-460 | $2.0 \times 10^{-12} \exp(-250/T)$ | |
| | Pastrana, Carr (1974) | 300 | $2.0 \pm 0.6 \times 10^{-13}$ | |
| | Davis, et al (1975) | 300 | $1.65 \pm 0.15 \times 10^{-13}$ | |

No recommendation

REFERENCES

- Davis, D. D., Fischer, S., Schiff, E., Watson, E. T., and Bollinger, W.,
 "A Kinetics Study of the Reaction of OH Radicals with Two C₂
 Hydrocarbons: C₂H₄ and C₂H₂," J. Chem. Phys. 63, 1707-1712 (1975)
 Pastrana, A., and Carr, E. W., Jr., "Rate of the Reaction of Hydroxyl
 Radical with Acetylene," Int. J. Chem. Kinet. 6, 587-595 (1974)
 Smith, I. W. M., and Zellner, E., "Rate Measurements of Reactions of OH by
 Resonance Absorption Part 2. Reactions of OH with CD₄, C₂H₄ and C₂H₂,"
 J. Chem. Soc., Faraday Trans. II 69, 1617-1627 (1973)
 P. F. Hampson
 May 1978

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Tempo Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncert. Factor at 298K, notes |
|-----|--------------------|------------------|--|----------------------------------|
|-----|--------------------|------------------|--|----------------------------------|

| | | | | | | | | | | | | | | | | | |
|-------|---|---------|--|------|---------|------|---|------|----|------|----|------|-----|------|-----|--|--|
| 19.57 | H ₂ + C ₂ H ₄ → products | | | | | | | | | | | | | | | | |
| | *Atkinson, Perry, Pitts (1977) | 299-425 | 2.2 x 10 ⁻¹² exp(385 ± 150/T) | | 1.3 (a) | | | | | | | | | | | | |
| | | | (a) High pressure values (225-660 torr Ar) Values also given for 25 and 75 torr pressure dependent values given over range 1 to 7 torr He 1.0 ± 0.2 x 10 ⁻¹¹ | | | | | | | | | | | | | | |
| | Rosard (1976) | 296 | | | (b) | | | | | | | | | | | | |
| | Gverend, Paraskevopoulos (1977) | 296 | (b) Authors' suggested limiting high pressure value based on expts at 400 torr SF ₆ and CF ₄ and analysis of dependence of k on [H ₂ O] at low values of [H ₂ O] | | | | | | | | | | | | | | |
| | Stuhl (1973c) | 298 | 3 x 10 ⁻¹² | | | | | | | | | | | | | | |
| | Smith, Zellner (1973) | 210-460 | 7.5 x 10 ⁻¹² exp(-110/T) | | | | | | | | | | | | | | |
| | Davis, et al (1975) | 300 | $\frac{10^{12} \cdot k}{P(\text{Hg})/\text{torr}}$ <table><tr><td>2.24</td><td>3</td></tr><tr><td>2.78</td><td>5</td></tr><tr><td>3.63</td><td>10</td></tr><tr><td>4.06</td><td>20</td></tr><tr><td>4.72</td><td>100</td></tr><tr><td>5.33</td><td>300</td></tr></table> | 2.24 | 3 | 2.78 | 5 | 3.63 | 10 | 4.06 | 20 | 4.72 | 100 | 5.33 | 300 | | |
| 2.24 | 3 | | | | | | | | | | | | | | | | |
| 2.78 | 5 | | | | | | | | | | | | | | | | |
| 3.63 | 10 | | | | | | | | | | | | | | | | |
| 4.06 | 20 | | | | | | | | | | | | | | | | |
| 4.72 | 100 | | | | | | | | | | | | | | | | |
| 5.33 | 300 | | | | | | | | | | | | | | | | |
| | | 300 | 3.64 x 10 ⁻¹² at 3 torr N ₂ | | | | | | | | | | | | | | |
| | Norris, et al (1971) | 300 | 1.8 x 10 ⁻¹² | | | | | | | | | | | | | | |
| | Bradley, et al (1973) | 300 | 1.7 ± 0.5 x 10 ⁻¹² | | | | | | | | | | | | | | |
| | Greiner (1970a) | 300-500 | 1.26 x 10 ⁻¹² exp(454/T) at 100 torr He | | | | | | | | | | | | | | |
| | Gordon, Mulec (1975) | 381 | 6.2 x 10 ⁻¹² (1 atm H ₂ O vapor) | | | | | | | | | | | | | | |
| | | 416 | 7.3 x 10 ⁻¹² (1 atm H ₂ O vapor) | | | | | | | | | | | | | | |

Recommendation is to use the temperature dependent results of Atkinson et al (1977) at high pressures. Within reliability factor given they are confirmed at room temperature by high pressure results of Gverend and Paraskevopoulos (1977)

REFERENCES

- Atkinson, R., Perry, R. A., and Pitts, J. N., Jr., "Rate Constants for the Reaction of OH Radicals with Ethylene over the Temperature Range 299-425°K," *J. Chem. Phys.* **66**, 1197-1201 (1977)
- Bradley, J. N., Back, W., Boyermann, R., and Wagner, R. G., "Kinetics of the Reaction of Hydroxyl Radicals with Ethylene and with C₃ Hydrocarbons," *J. Chem. Soc., Faraday Trans. I* **69**, 1869-1898 (1973)
- Davis, D., Fischer, S., Schiff, R., Watson, R. T., and Bollinger, W., "A Kinetic Study of the Reaction of OH Radicals with Two C₂ Hydrocarbons: C₂H₄ and C₂H₂," *J. Chem. Phys.* **53**, 1707-1712 (1975)
- Gordon, S., and Mulaic, R. A., "Reaction of the OH(X²Π) Radical Produced by the Pulse Radiolysis of Water Vapor," *Int. J. Chem. Kinet., Symp. No. 1*, 289-299 (1975)
- Greiner, R. R., "Hydroxyl Radical Kinetics by Kinetic Spectroscopy. VII. The Reaction with Ethylene in the Range 300-500°K," *J. Chem. Phys.* **53**, 1284-1285 (1970a)
- Howard, C. J., "Rate Constants for the Gas-Phase Reactions of OH Radicals with Ethylene and Halogenated Ethylene Compounds," *J. Chem. Phys.* **55**, 4771-4777 (1976)
- Morris, E. D., Jr., Stedman, D. R., and Niki, S., "Mass Spectrometric Study of the Reactions of the Hydroxyl Radical with Ethylene, Propylene, and Acetaldehyde in a Discharge-Flow System," *J. Amer. Chem. Soc.* **93**, 3570-3572 (1971)
- Gverend, R., and Paraskevopoulos, G., "Rates of OH Radical Reactions. III. The Reaction OH + C₂H₄ + M at 296°K," *J. Chem. Phys.* **62**, 674-679 (1977)
- Smith, I. W. M., and Zellner, R., "Rate Measurements of Reactions of OH by Resonance Absorption Part 2. Reactions of OH with CH₄, C₂H₄, and C₂H₂," *J. Chem. Soc., Faraday Trans. II* **69**, 1617-1627 (1973)
- Stuhl, F., "Determination of Rate Constants for the Reactions of OH with Propylene and Ethylene by a Pulsed Photolysis-Resonance Fluorescence Method," *Ber. Bunsenges. Physik. Chem.* **77**, 674-677 (1973c).

R. F. Hampson
May 1978

CHEMICAL KINETICS: DATA SURVEY

Reaction/Reference

Topic

Reaction Rate Constant
 $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

**Uncert. Factor
at 298K, notes**

| | | | |
|-------|---|---------|--------------------------------------|
| 19.58 | $\text{H}_2 + \text{C}_2\text{H}_6 \rightarrow \text{products}$ | | |
| | Greiner (1970) | 300-500 | $1.56 \times 10^{-11} \exp(-1230/T)$ |
| | Overend, et al (1975) | 300 | $2.64 \pm 0.17 \times 10^{-13}$ |
| | Howard, Evenson (1976b) | 296 | $(2.9 \pm 0.6) \times 10^{-13}$ |
| | | | 1.2 |

Recommendation is to use the results of the temperature dependent study by Greiner (1970). Room temperature value is in good agreement with the other reported results

REFERENCES

Greiner, N. P. "Hydroxyl Radical Kinetics by Kinetic Spectroscopy. VI. Reactions with Alkenes in the Range 300-500°K." *J. Chem. Phys.* **53**, 1070-1076 (1970)

Howard, C. J., and Evenson, K. M., "Rate Constants for the Reactions of OH with Ethane and some Halogen Substituted Ethanes at 296 K," *J. Chem. Phys.* **64**, 4303-4306 (1976b)

Overend, P., Paraskevopoulos, G., and Cvetanović, R. J., "Rates of OH Radical Reactions. I. Reactions with H_2 , CH_4 , C_2H_6 , and C_3H_8 at 295 K," *Can. J. Chem.* **53**, 3374-3382 (1975)

R. F. Hanson
May 1978

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Temp. Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncert. Factor at 298K, notes |
|-------|---|------------------|--|----------------------------------|
| 19.59 | H ₂ + C ₃ H ₆ → products | | | |
| | Atkinson, Pitts (1975b) | 297-425 | $4.1 \times 10^{-12} \exp(540 \pm 150/T)$ | 25-100 torr Ar |
| | Ravishankara, et al (1978) | 298 | $(2.56 \pm 0.12) \times 10^{-11}$ | 20 torr He |
| | | | $(2.63 \pm 0.12) \times 10^{-11}$ | 200 torr He |
| | Stuhl (1973c) | 298 | 1.45×10^{-11} | |
| | Morris, et al (1971) | 300 | 1.7×10^{-11} | |
| | Bradley, et al (1973) | 300 | $5.0 \pm 1.7 \times 10^{-12}$ | |
| | Gorse, Volman (1974) | 300 | k/(C ₂ H ₄ + H ₂) = 89.3 (low pressure) | |
| | | | k = 1.2×10^{-11} | (a) |
| | | | (a) k(C ₂ H ₄ + H ₂) = 1.4×10^{-13} , this survey | |
| | | 381 | 1.4×10^{-11} (1 atm H ₂ O vapor) | |
| | Gordon, Mulac (1975) | 416 | 2.0×10^{-11} (1 atm H ₂ O vapor) | |

Results of Atkinson and Pitts (1975b) are confirmed at room temperature by results of Ravishankara et al (1978)

REFERENCES

- Atkinson, R., and Pitts, J. N., Jr., "Rate Constants for the Reaction of OH Radicals with Propylene and the Butenes over the Temperature Range 297-425°K," J. Chem. Phys. **63**, 3591-3595 (1975b)
- Bradley, J. N., Back, W., Hoyermann, K., and Wagner, H. Gg., "Kinetics of the Reaction of Hydroxyl Radicals with Ethylene and with C₃ Hydrocarbons," J. Chem. Soc., Faraday Trans. I **69**, 1889-1898 (1973)
- Gordon, S., and Mulac, W. A., "Reaction of the OH(X²Π) Radical Produced by the Pulse Radiolysis of Water Vapor," Int. J. Chem. Kinet., Symp. No. 1, 289-299 (1975)
- Gorse, W. A., and Volman, D. E., "Photochemistry of the Gaseous Hydrogen Peroxide-Carbon Monoxide System II: Rate Constants for Hydroxyl Radical Reactions with Hydrocarbons and for Hydrogen Atom Reactions with Hydrogen Peroxide," J. Photochem. **3**, 115-122 (1974)

Morris, E. D., Jr., Stedman, D. H., and Niki, E., "Mass Spectrometric Study of the Reactions of the Hydroxyl Radical with Ethylene, Propylene, and Acetaldehyde in a Discharge-Flow System," *J. Amer. Chem. Soc.* **93**, 3570-3572 (1971)

Pavlenko, A. E., Wagner, S., Fischer, S., Smith, G., Schiff, H., Watson, R. Y., Teal, G., and Davis, D. D., "A Kinetic Study of the Reactions of OH with Several Aromatic and Olefinic Compounds," *Int. J. Chem. Kinet.* **10**, 783-804 (1978)

Stuhl, F., "Determination of Rate Constants for the Reactions of OH with Propylene and Ethylene by a Pulsed Photolysis-Resonance Fluorescence Method," *Ber. Bunsenges. Physik. Chem.* **77**, 674-677 (1973c).

E. F. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Uncertainty Factor
 at 298K, notes

| No. | Reaction/Reference | Temp. Range/K | Rate Constant $k/cm^3 \text{ molecule}^{-1} s^{-1}$ | Uncertainty Factor at 298K, notes |
|-------|---|------------------|--|--------------------------------------|
| 19,60 | $H_2 + n-C_4H_{10} \rightarrow \text{products}$ | | | |
| | Perry, Atkinson, Pitts (1976b) | 297-420 | $1.76 \times 10^{-11} \exp(-560/T)$ | 1.3 |
| | Greiner (1970) | 300-500 | $1.41 \times 10^{-11} \exp(-524/T)$ | |
| | Stuhl (1973b) | 300 | 2.35×10^{-12} | |
| | Gorme, Volman (1974) | 300 | $k/(CO + H_2) = 19.4$ (low pressure) | (a) |
| | | | $k = 2.7 \times 10^{-12}$ | |
| | | | (a) $k(CO + H_2) = 1.4 \times 10^{-13}$, this survey | |

Good agreement among all these values at room temperature

REFERENCES

Gorme, R. A., and Volman, D. E., "Photochemistry of the Gaseous Hydrogen Peroxide-Carbon Monoxide System II: Rate Constants for Hydroxyl Radical Reactions with Hydrocarbons and for Hydrogen Atom Reactions with Hydrogen Peroxide," *J. Photochem.* **3**, 115-122 (1974)

Greiner, W. R., "Hydroxyl Radical Kinetics by Kinetic Spectroscopy. VI. Reactions with Alkanes in the Range 300-500°K," *J. Chem. Phys.* **53**, 1070-1076 (1970)

Perry, R. A., Atkinson, R., and Pitts, J. N., Jr., "Rate Constants for the Reaction of OH Radicals with n-Butane over the Temperature Range 297-420°K," *J. Chem. Phys.* **64**, 5314-5316 (1976b)

Stuhl, F., "Rate Constant for the Reaction of OH with n-C₄H₁₀," *Z. Naturforsch.* **28a**, 1363-1364 (1973b)

R. F. Hampson
 May 1978

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS
Reaction Rate Constant
 $k/cm^3 \text{ molecule}^{-1} s^{-1}$

Uncert. Factor
at 298K, notes

| No. | Reaction/Reference | Temp. Range/K | $k/cm^3 \text{ molecule}^{-1} s^{-1}$ | Uncert. Factor at 298K, notes |
|-------|---|------------------|--|----------------------------------|
| 19,60 | HD + isobutane → products Greiner (1970) Gorse, Volman (1974) | 300-500 300 | $9.7 \times 10^{-12} \exp(-387/T)$ $k/(\text{HD} + \text{CD}) = 23.5$ $k = 3.3 \times 10^{-12}$ (low pressure) | (a) |
| | Butler, et al (1978) | 300 | (a) $k(\text{CD} + \text{CH}) = 1.4 \times 10^{-13}$, this survey 1.6×10^{-12} (b) Determined in expt. at 100 torr relative to $k(\text{HD} + \text{CD}) = 1.5 \times 10^{-13}$ | (b) |

No recommendation

REFERENCES

- Butler, R., Solomon, I. J., and Snelson, A., "Pressure Dependence of the
 $\text{CD} + \text{CH}$ Rate Constant in $\text{O}_2 + \text{N}_2$ Mixtures," *Chem. Phys. Lett.* **51**,
 19-24 (1978)
- Gorse, R. A., and Volman, D. E., "Photochemistry of the Gaseous Hydrogen
 Peroxide-Carbon Monoxide System II: Rate Constants for Hydroxyl Radical
 Reactions with Hydrocarbons and for Hydrogen Atom Reactions with Hydrogen
 Peroxide," *J. Photochem.* **3**, 115-122 (1974)
- Greiner, M. R., "Hydroxyl Radical Kinetics by Kinetic Spectroscopy. VI.
 Reactions with Alkanes in the Range 300-500°K," *J. Chem. Phys.* **53**,
 1070-1076 (1970)
- P. F. Hampson
 May 1978

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Reaction/Reference Temp. Reaction Rate Constant Uncertainty Factor
Range/K $k/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$ at 298K, notes

| | | | | |
|-------|--|---------|--|--|
| 19.00 | H ₂ + alkene - H ₂ O + alkyl radical Greiner (1970) | 300-500 | $k = [1.0 \exp(-820/T) M_p + 2.3 \exp(-430/T) M_s + 2.1 \exp(-95/T) M_t] \times 10^{-12}$ Where M_p , M_s , and M_t are the number of primary, secondary, and tertiary hydrogen atoms respectively. Do not use formula for CH ₄ and C ₂ H ₆ . | |
|-------|--|---------|--|--|

This additivity rule can be used to estimate the rate constant for the overall rate of hydrogen atom abstraction from an alkene by hydroxyl radical when there are no direct experimental data

REFERENCES

Greiner, N. R., "Hydroxyl Radical Kinetics by Kinetic Spectroscopy. VI. Reactions with Alkenes in the Range 300-500°K," J. Chem. Phys. **53**, 1073-1076 (1970)

P. F. Hampson
May 1976

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Temp. Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | | Uncertainty Factor at 298K, notes |
|--------|---|-----------------------|---|--|--------------------------------------|
| | | | | | |
| 19.60a | BD + C ₂ H ₆ - products | | | | |
| | Perry, Atkinson, Pitts (1977) | 298 380-470 298 | (1.20 ± 0.15) x 10 ⁻¹² k ₁ = 4 x 10 ⁻¹¹ exp(-2000/T) k ₁ /k = 0.05 | total rxn; P = 100 torr Ar (a) (b) | |
| | | | (a) k ₁ refers to abstraction rxn (b) Fraction of rxn preceding by abstraction; expression for k ₁ extrapolated to 298K | | |
| | Hansen, Atkinson, Pitts (1975) | 298 | (1.24 ± 0.12) x 10 ⁻¹² | total rxn; P = 50-600 torr Ar | |
| | Davis, Bollinger, Fischer (1975) | 298 | 0.85 x 10 ⁻¹² P = 3 torr He 1.36 x 10 ⁻¹² P = 20 torr He 1.59 x 10 ⁻¹² P = 100 torr He | total rxn total rxn total rxn | |

The results reported by Perry et al (1977) are the only temperature dependent data available. The room temperature value is in excellent agreement with the results of Hansen et al (1975) but 25% lower than the value of Davis et al (1975) at high pressure.

REFERENCES

- Davis, D. D., Bollinger, W., and Fischer, S., "A Kinetics Study of the Reaction of the CH Free Radical with Aromatic Compounds. I. Absolute Rate Constants for Reaction with Benzene and Toluene at 300°K," J. Phys. Chem. **79**, 293-294 (1975)
- Hansen, D. A., Atkinson, R., and Pitts, J. N., Jr., "Rate Constants for the Reaction of CH Radicals with a Series of Aromatic Hydrocarbons," J. Phys. Chem. **79**, 1763-1766 (1975)
- Perry, R. A., Atkinson, R., and Pitts, J. N., Jr., "Kinetics and Mechanism of the Gas Phase Reaction of CH Radicals with Aromatic Hydrocarbons over the Temperature Range 296-473 K," J. Phys. Chem. **81**, 296-304 (1977)

R. F. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS
Reaction/Reference Reaction Rate Constant
Temp. k/cm³ molecule⁻¹ s⁻¹
Range/K

Uncert. Factor
at 298K, notes

| No. | Reaction/Reference | Temp. Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncert. Factor at 298K, notes |
|--------|--|-----------------------|--|---|
| 19,60a | HO + C ₆ H ₅ CH ₃ → products Perry, Atkinson, Pitts (1977) | 298 360-470 298 | (6.40 ± 0.64) × 10 ⁻¹² k ₁ = 5 × 10 ⁻¹² exp(-450/T) k ₁ /k = 0.16 (a) k ₁ refers to H atom abstraction (b) Fraction of rxn proceeding by abstraction; expression for k ₁ extrapolated to 298K | total rxn; P = 200 torr Ar (a) (b) |
| | Hansen, Atkinson, Pitts (1975) Davis, Bollinger, Fischer (1975) | 298 298 | (5.78 ± 0.58) × 10 ⁻¹² 3.40 × 10 ⁻¹² P = 3 torr He 5.00 × 10 ⁻¹² P = 20 torr He 6.11 × 10 ⁻¹² P = 100 torr He | total rxn; P = 100-600 torr Ar total rxn total rxn total rxn |

The results reported by Perry et al (1977) are the only temperature dependent data available. The room temperature value is in good agreement with the other high pressure results

REFERENCES

- Davis, D. D., Bollinger, W., and Fischer, G., "A Kinetics Study of the Reaction of the CH Free Radical with Aromatic Compounds. I. Absolute Rate Constants for Reaction with Benzene and Toluene at 300°K," *J. Phys. Chem.* **79**, 293-294 (1975)
- Hansen, D. A., Atkinson, R., and Pitts, J. N., Jr., "Rate Constants for the Reaction of OH Radicals with a Series of Aromatic Hydrocarbons," *J. Phys. Chem.* **79**, 1763-1766 (1975)
- Perry, R. A., Atkinson, R., and Pitts, J. N., Jr., "Kinetics and Mechanism of the Gas Phase Reaction of OH Radicals with Aromatic Hydrocarbons Over the Temperature Range 296-473 K," *J. Phys. Chem.* **81**, 296-304 (1977)

R. F. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Uncertainty Factor
at 298K, notes

| No. | Reaction/Reference | Temp. Range/K | Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$ | Uncertainty Factor at 298K, notes |
|-------|---------------------------------------|------------------|---|--------------------------------------|
| 19.61 | $H_2 + CF_2Cl_2 \rightarrow$ products | | | |
| | NASA (1979) eval | 200-300 | $k < 1 \times 10^{-12} \exp(-3560/T)$ | (a) |
| | Atkinson, Hansen, Pitts (1975) | 257-424 | $k < 1 \times 10^{-15}$ | (a) |
| | Howard, Evenson (1976a) | 296 | $k < 4 \times 10^{-16}$ | (a) |
| | Chang, Kaufman (1977) | 480 | $k < 6 \times 10^{-16}$ | (a) |
| | Cox, et al (1976) | 252 | $k < 1 \times 10^{-16}$ | (a) |
| | | | (a) upper limit only | |

Unchanged from NASA 1010. The A-factor was estimated, and a lower limit derived for E/R by using the upper limits reported for the rate constants by Chang and Kaufman (1977) at ~ 480 K. These expressions are quite compatible with the upper limits reported for these rate constants by Atkinson et al (1975), Howard and Evenson (1976a), Cox et al (1976) and Clyne and Holt (1978). None of the investigators reported any evidence for reaction between OH and these chlorofluoromethanes

REFERENCES

Atkinson, R., Hansen, D. A., and Pitts, J. N., Jr., "Rate Constants for the Reaction of OH Radicals with CHF_2Cl , CF_2Cl_2 , $CFCl_3$, and H_2 over the Temperature Range 297-434°K," *J. Chem. Phys.* **63**, 1703-1706 (1975)

Chang, J. S., and Kaufman, F., "Upper Limits of the Rate Constants for the Reactions of $CFCl_3$ (P-11), CF_2Cl_2 (P-12), and H_2O with OH and Estimates of Corresponding Lower Limit of their Tropospheric Lifetimes," *Geophys. Res. Lett.* **4**, 152-154 (1977)

Clyne, M. A. A., and Holt, F., Private Communication, (1978)

Cox, R. A., Derwent, R. G., Eggleston, A. E. J., and Levelock, J. E., "Photochemical Oxidation of Halocarbons in the Troposphere," *Atmos. Environ.* **10**, 305-308 (1976)

Howard, C. J., and Evenson, K. M., "Rate Constants for the Reactions OH with CH_4 and Fluorine, Chlorine, and Bromine Substituted Methanes at 296 K," *J. Chem. Phys.* **64**, 197-202 (1976a)

NASA RP-1010. "Chlorofluoromethanes and the Stratosphere"
R. D. Hudson, Editor, August 1977 This reference contains
the NASA (1977) rate constant recommendations
NASA (1979). Recommendations of the NASA Panel for Data Evaluation,
published in NASA RP 1049 "The Stratosphere: Present and Future,"
R. D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the
June 1979 Harpers Ferry Workshop).
R. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Uncertainty Factor
at 298K, notes

| No. | Reaction/Reference | Temp. Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncertainty Factor at 298K, notes |
|-------|----------------------------------|------------------|--|--------------------------------------|
| | | | | |
| 19.62 | HF + CFC ₃ - products | | | |
| | NASA (1979) eval | 200-300 | $k < 1 \times 10^{-12}$ exp(-3650/T) | (a) |
| | Atkinson, Hansen, Pitts (1975) | 297-424 | $k < 1 \times 10^{-15}$ | (a) |
| | Howard, Evenson (1976a) | 256 | $k < 5 \times 10^{-16}$ | (a) |
| | Chang, Kaufman (1977) | 480 | $k < 5 \times 10^{-16}$ | (a) |
| | Cox, et al (1976) | 252 | $k < 1 \times 10^{-17}$ | (a) |
| | | | (a) upper limit only | |

Unchanged from NASA 1010. The A-factor was estimated, and a lower limit derived for E/E by using the upper limits reported for the rate constants by Chang and Kaufman (1977) at ~480 K. These expressions are quite compatible with the upper limits reported for these rate constants by Atkinson et al (1975), Howard and Evenson (1976a), Cox et al (1976) and Clyne and Holt (1978). None of the investigators reported any evidence for reaction between OH and these chlorofluoroethanes

REFERENCES

- Atkinson, R., Hansen, D. A., and Pitts, J. N., Jr., "Rate Constants for the Reaction of OH Radicals with CHF₂Cl, CF₂Cl₂, CFC₃, and H₂ over the Temperature Range 297-434°K," J. Chem. Phys. **63**, 1703-1706 (1975)
- Chang, J. S., and Kaufman, F., "Upper Limits of the Rate Constants for the Reactions of CFC₃(F-11), CF₂Cl₂(F-12), and N₂O with OH and Estimates of Corresponding Lower Limit of their Tropospheric Lifetimes," Geophys. Res. Lett. **4**, 192-194 (1977)
- Clyne, M. A. A., and Holt, F., Private Communication, (1978)
- Cox, R. A., Derwent, R. G., Eggleston, A. E. J., and Lovelock, J. E., "Photochemical Oxidation of Halocarbons in the Troposphere," Atmos. Environ. **10**, 305-308 (1976)
- Howard, C. J., and Evenson, K. M., "Rate Constants for the Reactions OH with CH₄ and Fluorine, Chlorine, and Bromine Substituted Methanes at 296 K," J. Chem. Phys. **54**, 197-202 (1976a)

NASA EP-1010. "Chlorofluoromethanes and the Stratosphere"
E. D. Hudson, Editor, August 1977 This reference contains
the NASA (1977) rate constant recommendations,
NASA (1979). Recommendations of the NASA Panel for Data Evaluation,
published in NASA EP 1049 "The Stratosphere: Present and Future."
E. D. Hudson and E. L. Reed, Editors, Dec. 1979 (report of the
June 1979 Barners Ferry Workshop).
E. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Uncertainty Factor
at 298K, notes

| No. | Reaction/Reference | Temp Range/K | Reaction Rate Constant $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | |
|-------|---|-----------------|--|---------------------|
| | | | $k \times 10^{-15}$ | $k \times 10^{-16}$ |
| 19.63 | $\text{H}_2 + \text{CCl}_4 \rightarrow \text{products}$ | 256 | (a) | (a) |
| | Howard, Evenson (1976a) | 258 | (a) | (a) |
| | Cox, et al (1976) | | (a) upper limit only | |

Note that these are upper limits only. No evidence for reaction was found

REFERENCES

- Cox, R. A., Derwent, R. G., Eggleston, A. E. Jr., and
Ivalock, J. E., "Photochemical oxidation of Halocarbons
in the Troposphere," Atmos. Environ. **10**, 305-308 (1976)
- Howard, C. J., and Evenson, L. M., "Rate Constants for the Reactions of H_2 with
 CH_4 and Fluorine, Chlorine, and Bromine Substituted Methanes at 296 K,"
J. Chem. Phys. **64**, 197-202 (1976a)

R. E. Hampson
May 1978

CHEMICAL KINETICS LATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Uncerto. Factor
at 298K, notes

Reaction/Reference

Temp.
Range/K

Reaction Rate Constant
 $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

No.

| | | | |
|-------|---|---------------------------------------|-------|
| 19.64 | $\text{H} + \text{CH}_3\text{Cl} \rightarrow \text{H}_2 + \text{CH}_2\text{Cl}$ | $\Delta H (298) = -74 \text{ kJ/mol}$ | |
| | NASA (1979) eval | 200-300 | 1.025 |
| | CODATA (1979) eval | 240-422 | 1.025 |
| | Davis, et al (1976) | 250-350 | |
| | Perry, Atkinson, Pitts (1976) | 298-423 | |
| | Howard, Evensen (1976a) | 296 | |

Unchanged from NASA 1010. The preferred values were obtained using only absolute rate coefficient data (Howard and Evensen (1976a), Davis et al (1976) and Perry et al (1976)). The studies (Davis et al (1975) and Butler et al (1978)) which determined $k(\text{H} + \text{CD}_3\text{Cl})$ are excluded until the kinetic behavior between $\text{H} + \text{CD}_3\text{Cl}$ is better understood, and the accuracy of the $\text{H} + \text{CH}_3\text{Cl}$ study (Cox et al (1976)) was probably no better than a factor of 2. Within the temperature range covered by Davis et al (1976) and Perry et al (298-400 K) the results agree to within 20%. However, the value of k obtained by using the Arrhenius expression of Perry et al at 240 K would be ~ 40% lower than the value obtained directly at that temperature by Davis et al (1976). The preferred value was obtained from a least squares fit to the data reported by Davis et al (1976) and Perry et al. Equal weighting was given to each of the bimolecular rate constants

REFERENCES

- Butler, R., Solomon, I. J., and Snelson, A., "Rate Constants for the Reaction of OH with Halocarbons in the Presence of $\text{O}_2 + \text{N}_2$," *J. Air Pollut. Control Assoc.* **28**, 1131-1133 (1978)
- CODATA(1979), Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.
- Cox, R. A., Derwent, R. G., Eggleston, A. E. J., and Lovelock, J. E., "Photochemical Oxidation of Halocarbons in the Troposphere," *Atmos. Environ.* **10**, 305-308 (1976)
- Davis, D. D., Hogan, P. E., and Gh, Y., 1975a, Results presented at the 4th CIAF Conference, Boston, February, (1975)
- Davis, D. D., Machado, G., Conway, B., Gh, Y., and Watson, R., "A Temperature Dependent Kinetics Study of the Reaction of OH with CH_3Cl , CH_2Cl_2 , CHCl_3 , and CH_3Br ," *J. Chem. Phys.* **65**, 1268-1274 (1976)

Howard, C. J., and Evenson, L. M., "Rate Constants for the Reactions OH with CH_4 and Fluorine, Chlorine, and Bromine Substituted Methanes at 296 K," J. Chem. Phys. **55**, 197-202 (1976a)

NASA RP-1010, "Chlorofluoromethanes and the Stratosphere"

W. D. Rudson, Editor, August 1977 This reference contains the NASA (1977) rate constant recommendations

NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," W. D. Rudson and E. L. Reed, Editors, Dec. 1979 (report of the June 1979 Harpers Ferry Workshop).

Perry, R. A., Atkinson, R., and Pitts, J. N., Jr., "Rate Constants for the Reaction of OH Radicals with CH_2Cl_2 and CH_3Cl over the Temperature Range 298-423°K. and with CH_2Cl_2 at 298°K," J. Chem. Phys. **54**, 1618-1620 (1976)

R. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS
Reaction/Reference Temp. Reaction Rate Constant Uncertainty Factor
No. Range/K k/cm³molecule⁻¹s⁻¹ at 298K, notes

| | | | | |
|-------|---|---------|--|------|
| 15.64 | HC + CH ₂ Cl ₂ → H ₂ O + CHCl ₂ | | | |
| | NASA (1979) eval | 200-300 | $5.5 \times 10^{-12} \exp(-10945/200/T)$ | 1.25 |
| | Davis, et al (1976) | 245-375 | $(4.27 \pm 0.63) \times 10^{-12} \exp(-1094 \pm 81/T)$ | |
| | Perry, Atkinson, Pitts (1976) | 252 | $(1.45 \pm 0.20) \times 10^{-13}$ | |
| | Howard, Evenson (1976a) | 256 | $(1.55 \pm 0.34) \times 10^{-13}$ | |

Minor modification to the A-factor from NASA 1010. The preferred values were obtained using only absolute rate coefficient data (Howard and Evenson (1976a), Davis et al (1976) and Perry et al (1976)). The accuracy of the $\text{CH} + \text{CH}_4$: $\text{CH} + \text{CH}_2\text{Cl}_2$ study (Cox et al (1976)) was probably no better than a factor of 2. The agreement at 298 K is good. The Arrhenius expression is based on the value of E/R reported by Davis et al, and an A-factor modified to fit the preferred value at 298K

REFERENCES

- Cox, R. A., Darwent, R. G., Eggleston, A. E. Jr., and Lovelock, J. E. "Photochemical Oxidation of Halocarbons in the Troposphere," Atmos. Environ. **10**, 305-302 (1976)
- Davis, D. D., Machado, G., Conaway, R. G., Y. C., and Watson, R. "A Temperature Dependent Kinetics Study of the Reaction of CH with CH_3Cl , CH_2Cl_2 , CHCl_3 , and CH_3Br ," J. Chem. Phys. **65**, 1268-1274 (1976)
- Howard, C. J., and Evenson, K. M., "Rate Constants for the Reactions CH with CH_4 and Fluorine, Chlorine, and Bromine Substituted Methanes at 296 K," J. Chem. Phys. **64**, 197-202 (1976a)

NASA RP-1010. "Chlorofluoromethanes and the Stratosphere"
R. D. Hudson, Editor, August 1977 This reference contains
the NASA (1977) rate constant recommendations
NASA (1979). Recommendations of the NASA Panel for Data Evaluation,
published in NASA RP 1049 "The Stratosphere: Present and Future,"
R. D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the
June 1979 Harpers Ferry Workshop).
Perry, R. A., Atkinson, R., and Pitts, J. N., Jr. "Rate Constants for the
Reaction of OH Radicals with CH_2Cl_2 and CH_3Cl over the Temperature
Range 298-423°K. and with CH_2Cl_2 at 298°K." J. Chem. Phys. 64,
1618-1620 (1976)
P. P. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Uncert. Factor
at 298K, notes

| No. | Reaction/Reference | Temp Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncert. Factor at 298K, notes |
|-------|---|-----------------|--|----------------------------------|
| 19,64 | RM + CCl ₃ → H ₂ + CCl ₃ | | ΔH (298) = - 98 kJ/mol | 1.25 |
| | NASA (1979) eval | 200-300 | 4.7 x 10 ⁻¹² exp(-(1134+200)/T) | |
| | Davis, et al (1976) | 245-375 | (4.69 ± 0.71) x 10 ⁻¹² exp(-1134 ± 108/T) | |
| | Howard, Evenson (1976a) | 296 | 1.01 ± 0.15 x 10 ⁻¹³ | |

Unchanged from NASA 1010. The preferred values were obtained using only absolute rate coefficient data (Howard and Evenson (1976a), and Davis et (1976)). The accuracy of the ΔH + CH_4 : CH_4 + $CHCl_3$ study (Cox et al (1976a)) was probably no better than a factor of 2. As the agreement at 298 K is excellent the preferred Arrhenius expression is that reported by Davis et al

REFERENCES

- Cox, R. A., Derwent, R. G., Eggleston, A. E. Jr., and Lovelock, J. R., "Photochemical Oxidation of Halocarbons in the Troposphere," *Atmos. Environ.* **10**, 305-308 (1976)
- Davis, D. D., Machado, G., Conway, R., Gh. Y., and Watson, R., "A Temperature Dependent Kinetics Study of the Reaction of CH_3Cl , CH_2Cl_2 , $CHCl_3$, and CH_3Br ," *J. Chem. Phys.* **55**, 1268-1274 (1976)
- Howard, C. J., and Evenson, K. M., "Rate Constants for the Reactions CH_4 with CH_4 and Fluorine, Chlorine, and Bromine Substituted Methanes at 296 K," *J. Chem. Phys.* **53**, 197-202 (1976a)
- NASA RP-1010, "Chlorofluoromethanes and the Stratosphere"
- R. D. Hudson, Editor, August 1977 This reference contains the NASA (1977) rate constant recommendations.
- NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future,"
- R. D. Hudson and R. I. Reed, Editors, Dec 1979 (report of the June 1979 Harper Ferry Workshop).

R. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS
Reaction/Reference Temp. Reaction Rate Constant
Range/K $k/cm^3 \text{ molecule}^{-1} s^{-1}$

Uncertainty Factor
at 298K, notes

| | | | | |
|-------|---|---------|--|------|
| 19.65 | $BC + C_2H_5Cl_2 \rightarrow H_2O + C_2H_5Cl$ | | $\Delta H (298) = -92 \text{ kJ/mol}$ | |
| | NASA (1979) eval | 200-300 | $1.5 \times 10^{-12} \exp(-(1184 \pm 200)/T)$ | 1.3 |
| | CODATA (1979) eval | 240-400 | $1.5 \times 10^{-12} \exp(-(1180 \pm 200)/T)$ | 1.25 |
| | Perry, Atkinson, Pitts (1976) | 298-422 | $1.75 \times 10^{-12} \exp(-1253 \pm 150/T)$ | |
| | Chang, Kaufman (1977) | 241-356 | $(1.16 \pm 0.17) \times 10^{-12} \exp(-1073 \pm 40/T)$ | |
| | Watson, et al (1977) | 245-375 | $(1.87 \pm 0.2) \times 10^{-12} \exp(-1245 \pm 26/T)$ | |
| | Howard, Evenson (1976a) | 296 | 2.6×10^{-14} | |
| | Clyne, Holt (1979) | 294-426 | $4.8 \times 10^{-12} \exp(-1400/T)$ | |

Changed from NASA 1010. The preferred values were derived using the data reported by Howard and Evenson (1976a), Watson et al (1977), Perry et al (1976) and Chang and Kaufman (1977). The data of Clyne and Holt (1979) was not considered as it is in rather poor agreement with the other data within the temperature range studied, e.g., there is a difference of ~ 65% at 400 K

REFERENCES

Chang, J. S., and Kaufman, F., "Kinetics of the Reactions of Hydroxyl Radicals with Some Halocarbons: CH_2Cl_2 , CH_2Cl_2 , CH_3CCl_3 , $C_2H_5Cl_3$, and C_2Cl_4 ," J. Chem. Phys. **66**, 4589-4994 (1977)

Clyne, W. A., and Holt, P. M., "Reaction Kinetics Involving Ground $X^2\Omega$ and Excited $A^2\Sigma^+$ Hydroxyl Radicals. Part 2. Rate Constants for Reactions of OH $X^2\Omega$ with Halogenomethanes and Halogenoethanes," J. Chem. Soc. Faraday Trans. II **75**, 582-591 (1979)

CODATA(1979). Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.

Howard, C. J., and Evenson, E. M., "Rate Constants for the Reactions of OH with CH_4 and Fluorine, Chlorine, and Bromine Substituted Methanes at 296 K," J. Chem. Phys. **64**, 197-202 (1976a)

NASA RP-1010. "Chlorofluoromethanes and the Stratosphere" E. D. Hudson, Editor, August 1977 This reference contains the NASA (1977) rate constant recommendations

NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA EP 1049 "The Stratosphere: Present and Future," R. D. Hudson and E. L. Reed, Editors, Dec. 1979 (report of the June 1979 Harpers Ferry Workshop).

Perry, R. A., Atkinson, R., and Pitts, J. N., Jr., "Rate Constants for the Reaction of OH Radicals with CH_2Cl_2 and CH_3Cl over the Temperature Range 298-423°K, and with CH_2Cl_2 at 298°K," *J. Chem. Phys.* **64**, 1618-1620 (1976)

Nelson, W. L., Machado, G., Conway, B., Wagner, S., and Davis, D. D., "A Temperature Dependent Kinetics Study of the Reaction of OH with CH_2Cl_2 , CHCl_3 , CH_2ClF , CHClF_2 , CH_3CCl_3 , $\text{CH}_3\text{CF}_2\text{Cl}$, and $\text{CF}_2\text{ClCFCl}_2$," *J. Phys. Chem.* **81**, 256-262 (1977)

G. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY
HYDROGEN DATA CENTER NATIONAL BUREAU OF STANDARDS

PREPARED AT CHEM
Reaction/Reference

Uncerto. Factor
at 298K, notes

| Ref. | Range/K | ΔH (298) = - 66 kJ/mol | ΔS (298) = - 66 kJ/mol |
|-------|---------|----------------------------------|--------------------------------|
| 19.65 | 200-300 | 1.2×10^{-12} | $\exp(-1666 \pm 200)/T$ |
| | 240-400 | 1.3×10^{-12} | $\exp(-1670 \pm 200)/T$ |
| | 297-434 | 1.21×10^{-12} | $\exp(-1636 \pm 150)/T$ |
| | 253-427 | $(1.20 \pm 1.0) \times 10^{-13}$ | $\exp(-1657 \pm 35)/T$ |
| | 250-350 | $(9.25 \pm 1.0) \times 10^{-13}$ | $\exp(-1575 \pm 71)/T$ |
| | 263-373 | 2.1×10^{-12} | $\exp(-1780 \pm 150)/T$ |
| | 296 | 3.4×10^{-15} | |
| | 29A-426 | 9.6×10^{-12} | $\exp(-2300 \pm 200)/T$ |

Minor modification from NASA 1010 due to new data. The values reported by Howard and Evenson (1976a), Watson et al (1977), Atkinson et al (1975), Chang and Kaufman (1977), Handwerk and Zellner (1978) and Clyne and Holt (1975) for K at 298 K are in good agreement. Consequently the preferred value is a simple mean of all the results.

However, the Arrhenius expression reported by Clyne and Holt is in very poor agreement with all other expressions, and as such the data reported by Clyne and Holt is not considered when deriving the preferred Arrhenius expression. The preferred Arrhenius expression was derived to best fit the data reported from all studies except that of Clyne and Holt.

REFERENCES

- Atkinson, P., Hansen, D. A., and Pitts, J. N., Jr., "Rate Constants for the Reaction of OH Radicals with CHF_2Cl , CF_2Cl_2 , CFCl_3 , and H_2 over the Temperature Range 297-434°K," *J. Chem. Phys.* **63**, 1703-1706 (1975)
- Chang, J. S., and Kaufman, F., "Kinetics of the Reactions of Hydroxyl Radicals with Some Halocarbons: CHFCl_2 , CF_2Cl_2 , CF_3CCl_3 , C_2HCl_3 , and C_2Cl_4 ," *J. Chem. Phys.* **56**, 4585-4594 (1977)
- Clyne, M. A. A., and Holt, P. M., "Reaction Kinetics Involving Ground X^2N and Excited A^2I^+ Hydroxyl Radicals: Part 2, Rate Constants for Reactions of OH X^2N with Halogenomethanes and Halogenoethanes," *J. Chem. Soc. Faraday Trans. II* **75**, 582-591 (1979)
- CCDATA(1979), Recommendations of the CCData Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.

Wanders, V., and Zellner, E., "Kinetics of the Reactions of OH Radicals with Some Halocarbons (CHClF_2 , CH_2ClF , CH_2ClCF_3 , CH_3CClF_2 , CH_3CHF_2) in the Temperature Range 260-370 K," *J. Phys. Chem.* **82**, 1161-1166 (1978)

Howard, C. J., and Evensen, K. M., "Rate Constants for the Reactions OH with CH_4 and Fluorine, Chlorine, and Bromine Substituted Methanes at 296 K," *J. Chem. Phys.* **83**, 197-202 (1976a)

NASA RP-1010, "Chlorofluoromethanes and the Stratosphere"

R. D. Hudson, Editor, August 1977 This reference contains the NASA (1977) rate constant recommendations

NASA (1979), Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future,"

R. D. Hudson and E. I. Reed, Editors, Dec 1979 (report of the June 1979 Harpers Ferry Workshop).

Batson, R. L., Machado, G., Conway, B., Wagner, S., and Davis, D. D., "A Temperature Dependent Kinetics Study of the Reaction of OH with CH_2ClF , CHCl_2 , CHClF_2 , CH_3CCl_3 , $\text{CH}_3\text{CF}_2\text{Cl}$, and $\text{CF}_2\text{ClCFCl}_2$," *J. Phys. Chem.* **81**, 256-262 (1977)

V. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY
 PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Uncerto. Factor
at 298K, notes

| No. | Reaction/Reference | Temp. Range/K | Rate Constant $k/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$ | Uncerto. Factor at 298K, notes |
|-------|--|------------------|---|-----------------------------------|
| 19.65 | $\text{H} + \text{CH}_2\text{FCl} \rightarrow \text{H}_2 + \text{CHFCl}$ | | | |
| | NASA (1979) eval | 200-300 | $3.5 \times 10^{-12} \exp(-13220/150)/T$ | 1.25 |
| | Watson, et al (1977) | 245-375 | $(2.84 \pm 0.3) \times 10^{-12} \exp(-1259 \pm 50/T)$ | |
| | Howard, Evenson (1976a) | 296 | $3.7 \pm 0.6 \times 10^{-14}$ | |
| | Handwerk, Zellner (1978) | 273-373 | $3.1 \times 10^{-12} \exp(-13200/100)/T$ | |

Minor modification from NASA 1010 due to new data. The 298 K values reported by Howard and Evenson (1976a), Watson et al (1977) and Handwerk and Zellner (1978) are in good agreement and have been averaged to obtain the preferred 298 K value. The Arrhenius expression of Watson et al and Handwerk and Zellner are in excellent agreement. The preferred Arrhenius parameters were obtained from a least squares treatment of all published data

REFERENCES

- Handwerk, V., and Zellner, P., "Kinetics of the Reactions of OH Radicals with Some Halocarbons (CHClF_2 , CH_2ClF , CH_2ClCF_3 , CH_3CClF_2 , CH_3CHF_2) in the Temperature Range 260-370 K," Ber. Bunsenges. Phys. Chem. **82**, 1161-1166 (1978)
- Howard, C. J., and Evenson, E. M., "Rate Constants for the Reactions OH with CH_4 and Fluorine, Chlorine, and Bromine Substituted Methanes at 296 K," J. Chem. Phys. **61**, 197-202 (1976a)
- NASA RP-1010, "Chlorofluoromethanes and the Stratosphere" E. D. Hudson, Editor, August 1977 This reference contains the NASA (1977) rate constant recommendations.

NASA (1979). Recommendations of the NASA Panel for Data Evaluation,
published in NASA SP 1049 "The Stratosphere: Present and Future,"
R. D. Hudson and E. I. Reed, Editors, Dec. 1975 (report of the
June 1979 Harpers Ferry Workshop).
Bateon, R. T., Machado, G., Conway, B., Wagner, S., and Davis, D. D.,
"A Temperature Dependent Kinetics Study of the Reaction of OH with
CH₂ClF, CHCl₂F, CHClF₂, CH₃CCl₃, CH₃CF₂Cl, and CF₂ClCFCF₂Cl,"
J. Phys. Chem. **81**, 256-262 (1977).
R. P. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Reaction/Reference
Temp.
Range/K
Reaction Rate Constant
 $k/\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$
Uncert. Factor
at 298K, notes

| | | | | |
|-------|--|-----|--------------------------------|--|
| 19.65 | $\text{H} + \text{CH}_3\text{F} \rightarrow \text{products}$ | | | |
| | Howard, Evenson (1976a) | 296 | $(16 \pm 3.5) \times 10^{-15}$ | |

No recommendation

REFERENCES

Howard, C. J., and Evenson, K. M., "Rate Constants for the Reactions of H with CH_4 and Fluorine, Chlorine, and Bromine Substituted Methanes at 296 K,"
J. Chem. Phys. 64, 197-202 (1976a)

F. P. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Uncertainty Factor
at 298K, notes

Reaction/Reference Test
Range/K Reaction Rate Constant
k/cm³molecule⁻¹s⁻¹

No.

19.65 $\text{F}^\bullet + \text{CH}_2\text{F}_2 \rightarrow \text{products}$
 Clyne, Holt (1975)
 Howard, Evenson (1976a)

253-425
256

$7.4 \times 10^{-12} \exp(-2100/T)$
 $(7.8 \pm 0.2) \times 10^{-15}$

The results reported by Clyne and Holt (1975) are the only temperature dependent data available.
 The two room temperature values are in good agreement.

REFERENCES

Clyne, W. A. A., and Holt, P. M., "Reaction Kinetics Involving Ground X^2N and Excited A^2I Hydroxyl Radicals. Part 2: Rate Constants for Reactions of $\text{OH X}^2\text{N}$ with Halogenomethanes and Halogenoethanes," J. Chem. Soc. Faraday Trans. II **75**, 582-591 (1975)
 Howard, C. J., and Evenson, K. M., "Rate Constants for the Reactions OH with CH_4 and Fluorine, Chlorine, and Bromine Substituted Methanes at 296 K," J. Chem. Phys. **64**, 197-202 (1976a)

P. F. Hampson
 June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS
Reaction/Reference

Uncertainty Factor
at 298K, notes

| No. | Reaction/Reference | Temp Range/K | Reaction Rate Constant $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | Uncertainty Factor at 298K, notes |
|-------|---|-----------------|--|--------------------------------------|
| 19,65 | $\text{H} + \text{CHF}_3 \rightarrow \text{products}$ | | | |
| | Boward, Evenson (1976a) | 256 | 2×10^{-16} | |
| | Clyne, Holt (1975) | 296-430 | $(1.3 \pm 0.7) \times 10^{-15}$ | |

No recommendation

REFERENCES

- Clyne, W. A. A., and Holt, P. M., "Reaction Kinetics Involving Ground X^2H and Excited A^2I^+ Hydroxyl Radicals. Part 2: Rate Constants for Reactions of OH X^2H with Halogenomethanes and Halogenoethanes," J. Chem. Soc. Faraday Trans. II 75, 582-591 (1975)
- Boward, C. J., and Evenson, K. M., "Rate Constants for the Reactions OH with CH_4 and Fluorine, Chlorine, and Bromine Substituted Methanes at 296 K," J. Chem. Phys. 64, 197-202 (1976a)
- P. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Uncertainty Factor
at 298K, notes

| No. | Reaction/Reference | Temp Range/K | Reaction Rate Constant $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | Uncertainty Factor at 298K, notes |
|-------|--|-----------------|--|--------------------------------------|
| 19,65 | HC + CF ₄ → products Booard, Evenson (1976a) | 256 | $k < 4 \times 10^{-16}$ | upper limit only |

No recommendation

REFERENCES

Booard, C. J., and Evenson, K. M., "Rate Constants for the Reactions of H with
CF₄ and Fluorine, Chlorine, and Bromine Substituted Methanes at 296 K,"
J. Chem. Phys. **64**, 157-202 (1976a)

P. F. Hampson
May 1976

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Uncerto Factor
at 298K, notes

Reaction/Reference
Tempo
Range/K
Reaction Rate Constant
k/cm³ molecule⁻¹ s⁻¹

No.

19,65

H₂ + CF₃Cl - Products

Howard, Evenson (1976a)

296

k = 7 x 10⁻¹⁶

upper limit only

No recommendation

REFERENCES

Howard, Co. J., and Evenson, K. M., "Rate Constants for the Reactions CH with
CH₄ and Fluorine, Chlorine, and Bromine Substituted Methanes at 296 K,"
J. Chem. Phys. 64, 197-202 (1976a)

R. F. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Uncert. Factor
at 298K, notes

| No. | Reaction/Reference | Temp. Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncert. Factor at 298K, notes |
|-------|---|------------------|--|----------------------------------|
| 19,65 | NO + CH ₃ Br → H ₂ O + CH ₂ Br | | ΔH (298) = - 80 kJ/mol | |
| | NASA (1979) eval | 200-300 | 7.9 x 10 ⁻¹³ exp(-(889±200)/T) | 1.25 |
| | CODATA (1979) eval | 244-350 | 7.6 x 10 ⁻¹³ exp(-(890±200)/T) | 1.25 |
| | Davis, et al (1976) | 245-350 | (7.93 ± 0.79) x 10 ⁻¹³ exp(-(889±58)/T) | |
| | Howard, Evenson (1976a) | 256 | (3.5±0.8) x 10 ⁻¹⁴ | |

Unchanged from NASA 1010. The preferred value of 298 K is the mean of the two results (Howard and Evenson (1976a) and Davis et al (1976) which are in excellent agreement. The A-factor of the Arrhenius expression looks a little low considering that there are three abstractable hydrogen atoms (the Arrhenius expression is that reported by Davis et al)

REFERENCES

- CODATA(1979), Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.
- Davis, D. D., Machado, G., Conway, B., Gh, Y., and Watson, E., "A Temperature Dependent Kinetics Study of the Reaction of OH with CH₃Cl, CH₂Cl₂, CCl₃, and CH₃Br," J. Chem. Phys. **65**, 1268-1274 (1976)
- Howard, C. J., and Evenson, I. M., "Rate Constants for the Reactions OH with CH₄ and Fluorine, Chlorine, and Bromine Substituted Methanes at 296 K," J. Chem. Phys. **64**, 197-202 (1976a)
- NASA RP-1010, "Chlorofluoromethanes and the Stratosphere"
- E. D. Hudson, Editor, August 1977 This reference contains the NASA (1977) rate constant recommendations.
- NASA (1979), Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future."
- E. D. Hudson and E. I. Reed, Editors, Dec. 1975 (report of the June 1975 Harpers Ferry Workshop)
- P. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No | Reaction/Reference | Temp. Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncert. Factor at 298K, notes |
|-------|---|------------------|--|----------------------------------|
| | | | | |
| 19,05 | H ₂ + CH ₃ CCl ₃ → H ₂ O + CH ₂ CCl ₃ | | ΔH (298) = - 94 kJ/mol | |
| | MARA (1979) eval | 200-300 | 5.4 x 10 ⁻¹² exp(-(1820±200)/T) | 1-3 |
| | CODATA (1979) eval | 250-460 | 5.1 x 10 ⁻¹² exp(-(1800±200)/T) | 1-4 |
| | Kurylo, et al (1979) | 253-363 | (5.8±1.0) x 10 ⁻¹² exp(-(1810±100)/T) | |
| | Jeong, Kaufman (1979) | 278-460 | (5.8±1.4) x 10 ⁻¹² exp(-(1830±100)/T) | |
| | Clyne, Holt (1975) | 253-430 | (2.4±0.8) x 10 ⁻¹² exp(-(1394±113)/T) | |
| | Watson, et al (1977) | 260-375 | (3.72±0.4) x 10 ⁻¹² exp(-1627±59/T) | |
| | Chang, Kaufman (1977) | 275-405 | (1.95±0.24) x 10 ⁻¹² exp(-1333±37/T) | |
| | Howard, Evenson (1976b) | 296 | (15±3) x 10 ⁻¹⁵ | |

This evaluation is based on the recent data of Kurylo et al (1979) and Jeong and Kaufman (1979). Their results are in excellent agreement. The earlier result of Howard and Evenson (1976b), Watson et al (1977), Chang and Kaufman (1977) and Clyne and Holt (1975) are rejected in favor of the recent results. The CH₃CCl₃ used in the early studies may have been contaminated.

REFERENCES

- Chang, J. S., and Kaufman, F., "Kinetics of the Reactions of Hydroxyl Radicals with Some Halocarbons: CH₂Cl₂, CHF₂Cl, CH₃CCl₃, C₂HCl₃, and C₂Cl₄," J. Chem. Phys. **66**, 4989-4994 (1977)
- Clyne, M. A., and Holt, P. M., "Reaction Kinetics Involving Ground I² and Excited A²Σ⁺ Hydroxyl Radicals. Part 1: Quenching Kinetics of OH A²Σ⁺ and Rate Constants for Reactions of OH I² with CH₃CCl₃ and C₆," J. Chem. Soc., Faraday Trans. II **75**, 565-581 (1979)
- CODATA(1979): Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.
- Howard, C. J., and Evenson, K. M., "Rate Constants for the Reactions of OH with Ethane and some Halogen Substituted Ethanes at 296 K," J. Chem. Phys. **64**, 4303-4306 (1976b)
- Jeong, K. M., and Kaufman, F., "Rates of the Reactions of 1,1,1-Trichloroethane (Methyl Chloroform) and 1,1,2-Trichloroethane with OH," *Geophys. Res. Lett.* in press (1979)

Kurylo, M. J., Anderson, P. G., and Klein, G., "A Flash Photolysis Resonance Fluorescence Investigation of the Reaction $\text{OH} + \text{CH}_3\text{CCl}_3 \rightarrow \text{H}_2\text{O} + \text{CH}_2\text{CCl}_3$," *Geophys. Res. Lett.* in press (1979)

NASA (1979), Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future,"

R. D. Hudson and R. L. Reed, Editors, Deco 1979 (report of the June 1975 Harpers Ferry Workshop)

Satman, E. Z., Machado, G., Conway, R., Wagner, S., and Davis, D. D., "A Temperature Dependent Kinetics Study of the Reaction of OH with CH_2ClF , CHCl_2F , CHClF_2 , CH_3CCl_3 , $\text{CH}_3\text{CF}_2\text{Cl}$, and $\text{CH}_2\text{ClCFCl}_2$," *J. Phys. Chem. A*, 256-262 (1977)

R. P. Haysen
June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Reaction/Reference
Tempo
Range/K
Reaction Rate Constant
 $k/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$
Uncert. Factor
at 298K, notes

| No. | Reaction/Reference | Tempo Range/K | Reaction Rate Constant $k/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$ | Uncert. Factor at 298K, notes |
|-------|--|------------------|--|----------------------------------|
| 19.65 | $\text{NO} + \text{C}_2\text{HCl}_3 \rightarrow \text{products}$ | | | |
| | NASA (1979) eval | 200-300 | $5.0 \times 10^{-13} \exp((445 \pm 200)/T)$ | 1.25 |
| | Chang, Kaufman (1977) | 234-420 | $(5.32 \pm 0.71) \times 10^{-13} \exp((445 \pm 41)/T)$ | |
| | Davis, et al (1978) | 300 | $(2.35 \pm 0.25) \times 10^{-12}$ | preliminary |
| | Howard (1976) | 256 | $(2.0 \pm 0.4) \times 10^{-12}$ | |

Changed from NASA 1010 which recommended a temperature independent value. The results of the three absolute rate coefficient studies (Howard (1976), Chang and Kaufman (1977) and Davis et al (1978) are in excellent agreement at 298 K. The value derived from a relative rate coefficient study by Winer et al (1976) is a factor of ~ 2 greater than the other values and is not considered in deriving the preferred value at 298 K. The Arrhenius parameters are those reported by Chang and Kaufman

REFERENCES

- Chang, J. S., and Kaufman, F., "Kinetics of the Reactions of Hydroxyl Radicals with Some Halocarbons: CH_2Cl_2 , CHF_2Cl , CH_3OCCl_3 , C_2HCl_3 , and C_2Cl_4 ," J. Chem. Phys. **56**, 4589-4994 (1977)
- Davis, D. D., Machado, U. Smith, G., Wagner, S., and Watson, R. T., Manuscript in preparation, (1978)
- Howard, C. J., "Rate Constants for the Gas-Phase Reactions of OH Radicals with Ethylene and Halogenated Ethylene Compounds," J. Chem. Phys. **55**, 4771-4777 (1976)
- NASA EP-1010, "Chlorofluoromethanes and the Stratosphere" by D. Hudson, Editor, August 1977 This reference contains the NASA (1977) rate constant recommendations.

NASA (1979). Recommendations of the NASA Panel for Data Evaluation,
published in NASA RP 1049 "The Stratosphere: Present and Future,"
R. D. Hudson and E. L. Reed, Editors, Dec. 1979 (report of the
June 1975 Harpers Ferry Workshop).

Biner, A. M., Lloyd, A. C., Darnall, E. W., and Pitts, J. N. Jr.,
"Relative Rate Constants for the Reaction of the
Hydroxyl Radical with Selected Ketones, Chloroethenes,
and Monoterpene Hydrocarbons," J. Phys. Chem. 80,
1635-1635 (1976)

E. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Temp. Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncert. Factor at 298K, notes |
|-------|--|------------------|--|----------------------------------|
| | | | | |
| 15.65 | BC + C ₂ Cl ₄ - products | | | |
| | NASA (1979) eval | 200-300 | $9.4 \times 10^{-12} \exp(-(1199 \pm 200)/T)$ | 1.25 |
| | Chang, Kaufman (1977) | 297-420 | $(9.44 \pm 1.34) \times 10^{-12} \exp(-(1199 \pm 55)/T)$ | |
| | Davis, et al (1978) | 260-375 | $(1.06 \pm 0.5) \times 10^{-11} \exp(-(1300 \pm 150)/T)$ | preliminary |
| | Howard (1976) | 296 | $(1.70 \pm 0.34) \times 10^{-13}$ | |

Unchanged from NASA 1010. The preferred value at 298 K is a mean of the values reported by Howard (1976), Chang and Kaufman (1977) and Davis et al (1978). As these values are in excellent agreement (better than 10%), the value reported by Winer et al (1976) which is more than a factor of 10 greater must be rejected. The results of the temperature dependence studies reported by Chang and Kaufman, and Davis et al are in excellent agreement (better than 30% at all temperatures between 220 and 425 K). The preferred Arrhenius parameters are those of Chang and Kaufman as the data of Davis et al has yet to be published

REFERENCES

- Chang, J. S., and Kaufman, F., "Kinetics of the Reactions of Hydroxyl Radicals with Some Halocarbons: CH₃Cl, CH₂Cl₂, CH₃CCl₃, C₂HCl₃, and C₂Cl₄," J. Chem. Phys. **66**, 4969-4994 (1977)
- Davis, D. D., Machado, U., Smith, G., Wagner, S., and Watson, R. T., Manuscript in preparation, (1978)
- Howard, C. J., "Rate Constants for the Gas-Phase Reactions of OH Radicals with Ethylene and Halogenated Ethylene Compounds," J. Chem. Phys. **65**, 4771-4777 (1976)
- NASA RP-1010, "Chlorofluoromethanes and the Stratosphere" R. D. Hudson, Editor, August 1977 This reference contains the NASA (1977) rate constant recommendations.

NASA (1979). Recommendations of the NASA Panel for Data Evaluation.
published in NASA EP 1049 "The Stratosphere: Present and Future."
R. D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the
June 1979 Harpers Ferry Workshop).

Winer, A. M., Lloyd, A. C., Darnall, K. R., and Pitta, J. M. Jr.,
"Relative Rate Constants for the Reaction of the
Hydroxyl Radical with Selected Ketones, Chloroethenes,
and Monoterpene Hydrocarbons," J. Phys. Chem. **80**,
1635-1638 (1976)

P. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Uncerto Factor
at 258K, notes

| No. | Reaction/Reference | Temp. Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncerto Factor at 258K, notes |
|-------|--|------------------|--|----------------------------------|
| 19.65 | H ₂ + CH ₃ CF ₂ Cl → products | | | |
| | This survey | 275-375 | 1.5 x 10 ⁻¹² exp(-1800/T) | 1.3 |
| | Watson, et al (1977) | 273-375 | 1.15 x 10 ⁻¹² exp(-(1748±30)/T) | |
| | Clyne, Holt (1979) | 293-417 | 3.3 x 10 ⁻¹² exp(-(1800±300)/T) | |
| | Handwerk, Zellner (1978) | 293-373 | 1.8 x 10 ⁻¹² exp(-(1790±150)/T) | |
| | Howard, Evenson (1976t) | 296 | (2.8±0.4) x 10 ⁻¹⁵ | |

Recommended expression accepts the reported temperature dependence and averages the room temperature values except for the value of Clyne and Holt (1979) which is much higher than the others

REFERENCES

Clyne, M. A. A., and Holt, P. M., "Reaction Kinetics Involving Ground X²Π and Excited A²Σ⁺ Hydroxyl Radicals. Part 2: Rate Constants for Reactions of OH X²Π with Halogenomethanes and Halogenoethanes," *J. Chem. Soc., Faraday Trans. II* **75**, 582-591 (1979)

Handwerk, V., and Zellner, R., "Kinetics of the Reactions of OH Radicals with Some Halocarbons (CHClF₂, CH₂ClF, CH₂ClCF₃, CH₃CClF₂, CH₃CHF₂) in the Temperature Range 260-370 K," *Ber. Bunsenges. Phys. Chem.* **82**, 1161-1166 (1978)

Howard, C. J., and Evenson, K. M., "Rate Constants for the Reactions of OH with Ethane and some Halogen Substituted Ethanes at 296 K," *J. Chem. Phys.* **64**, 4303-4306 (1976b)

Watson, R. L., Machado, G., Conway, B., Wagner, S., and Davis, D. D., "A Temperature Dependent Kinetics Study of the Reaction of OH with CH₂ClF, CHCl₂F, CHClF₂, CH₃CCl₃, CH₃CF₂Cl, and CF₂ClCFCl₂," *J. Phys. Chem.* **81**, 256-262 (1977)

R. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Temp. | | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncertainty Factor at 298K, notes |
|--------|---|---------|---------------------------|--|--------------------------------------|
| | | Range/K | | | |
| 19, 65 | H ₂ + CF ₂ ClCFCl ₂ → products | | | | |
| | Watson, et al (1977) | 258 | k = 3 x 10 ⁻¹⁶ | (a) | |
| | Howard, Evenson (1976) | 256 | k = 3 x 10 ⁻¹⁶ | (a) | |
| | | | (a) upper limit only | | |

Note that these are upper limits only. No evidence for reaction was found

REFERENCES

- Watson, R. To, Machado, G., Conway, B., Wagner, S., and Davis, D. D.,
 "A Temperature Dependent Kinetics Study of the Reaction of OH with
 CH₂ClF, CHClF₂, CHClF₂, CH₃CCl₃, CH₃CF₂Cl, and CF₂ClCFCl₂,"
 J. Phys. Chem. **81**, 256-262 (1977)
- Howard, C. J., and Evenson, K. M., "Rate Constants for the Reactions of OH
 with Ethane and some Halogen Substituted Ethanes at 296 K," J. Chem
 Phys. **64**, 4303-4306 (1976b)
- R. F. Hampson
 May 1976

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No | Reaction/Reference | Temp Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncert Factor at 298K, notes |
|--------|--|-----------------|--|---------------------------------|
| 2C, 2C | H ₂ + H ₂ O ₂ → 2H ₂ O NASA (1979) eval | 200-300 | ΔH (298) = -140 kJ/mol 2.5 x 10 ⁻¹² A(E/R) = 0, -1245 | 2 |
| | CMDATA (1979) eval | 298 | 2.3 x 10 ⁻¹² | 2 |
| | Hamilton, LII (1977) | 298 | 2.5 x 10 ⁻¹² | |
| | Cox (1978) | 273-338 | 3.8 x 10 ⁻¹⁴ exp(1245/T) | |
| | Burrows, et al (1978) | 298 | k = 1 x 10 ⁻¹² | P = 1 atm |
| | Baulch, et al (1972) review | 300 | 3.3 x 10 ⁻¹² | P = 2 torr |

This is the room temperature value of Hamilton and LII (1977) and Cox (1978). Both studies found the rate constant to be sensitive to the presence of water vapor (at the torr level). There is preliminary evidence in the Cox study for a very strong negative temperature dependence (E/R = -1245K) although the data are very limited. However, there is evidence that the strong τ dependence is not present at lower pressures. Thus, for the time being, E/R = 0, with a lower uncertainty bound of -1245K is recommended. Preliminary evidence of a pressure dependence (Burrows et al, 1978; Cox, 1978) would, if confirmed, require a further change in the recommendation. Recent measurements of the relevant rate constant ratios in a study by DeMore (1979) are consistent with both the water vapor and temperature effects cited by Cox.

REFERENCES

- Baulch, D. L., Drysdale, D. D., Horne, D. G., and Lloyd, A. G., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 1: Homogeneous Gas Phase reactions of the H₂-O₂ System," (Butterworths, London, 1972)
- Burrows, J. P., Cliff, D. L., Harris, G. W., Thrush, B. A., and Wilkinson, J. F. I., paper presented at WMO Symposium on Ozone, Toronto, June, (1978)
- CMDATA(1979), Recommendations of the CMDATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.
- Cox, R. A., 1978a, Paper presented at WMO Symposium on Ozone, Toronto, June, (1978)
- DeMore, W. B., "Reaction of H₂O₂ with O₃ and the Effect of Water Vapor on H₂O₂ Kinetics," J. Phys. Chem. **83**, 1113-1118 (1979)

Hamilton, E. J., Jr., and Hill, E.-E., "The Dependence on H_2 and on NH_3 of the Kinetics of the Self-Reaction of H_2 in the Gas-Phase. Formation of H_2 , H_2 and H_2 - NH_3 Complexes, Int. J. Chem. Kinet. 2, 875-885 (1977) NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," R. D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the June 1979 Harpers Ferry Workshop).

R. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY

Prepared at CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS
Reaction Rate Constant
k/cm³ molecule⁻¹ s⁻¹
Uncert. Factor
at 298K, notes

Temp
Range/K

ΔH (298) = - 62 kJ/mol
No recommendation
9 x 10⁻¹⁶
Relative to k (H₂ + H₂)
k < 1 x 10⁻¹⁸
Relative to k (H₂ + NO₂)

No recommendation

REFERENCES

- CMDATA(1979). Recommendations of the CMDATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.
- Graham, R. A., Winer, A. M., Atkinson, R., and Pitts, J. N., Jr., "Rate Constants for the Reaction of H₂ with H₂, S₂, O₃, N₂O, trans-2-Butene, and 2,3-Dimethyl-2-butene at 300 K," J. Phys. Chem. **83**, 1563-1567 (1979)
- Payne, W. A., Stief, L. J., and Davis, D. D., "A Kinetics Study of the Reaction of H₂ with S₂ and H₂, J. Amer. Chem. Soc. **95**, 7614-7619 (1973)
- R. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Uncert Factor
at 298K, notes

| No | Reaction/Reference | Temp. Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncert Factor at 298K, notes |
|-------|--|------------------|--|---------------------------------|
| 20,35 | H ₂ + Cl → HCl + d ₂ | | | |
| | NASA (1979) eval | | | |
| | CODATA (1979) eval | 200-300 | 4.5 x 10 ⁻¹¹ | 1-6 |
| | Leu, DeMore (1976) | 298 | 4.1 x 10 ⁻¹¹ | 2 |
| | Poulet, et al (1978) | 298 | 3 x 10 ⁻¹¹ | |
| | Burrows, et al (1978) | 293 | 6.8 x 10 ⁻¹¹ | |
| | Cox, Derwent (1977) | 306 | 4.1 x 10 ⁻¹¹ | |
| | | | 2.5 x 10 ⁻¹¹ | |

ΔH (298) = -216 kJ/mol

Changed from NASA 1010: The values of $k(\text{Cl} + \text{H}_2\text{O}_2)/k(\text{Cl} + \text{H}_2\text{O})$ reported by Leu and DeMore (1976), Poulet et al (1978), and Burrows et al (1978) are in poor agreement. The discrepancy between the two mass-spectrometric results may be attributed to inaccurate estimations of the mass-spectrometric sensitivity for H₂. If the NASA preferred value of 4.7×10^{-13} for $k(\text{Cl} + \text{H}_2\text{O}_2)$ at 298 K is combined with the experimentally determined ratios, then values of 2-3, 8-0 and $4-9 \times 10^{-11}$ are obtained for $k(\text{Cl} + \text{H}_2\text{O})$. The preferred value was obtained by averaging these three "re-evaluated" values with the value reported by Cox and Derwent (1977). The temperature dependence for such an atom-radical process is expected to be weak. Based upon the data reported by Burrows et al (1978) an upper limit of 4.5×10^{-13} has been placed on the rate constant for production of ClO + OH (1% total rate constant)

REFERENCES

- Burrows, J. P., Cliff, D. I., Harris, G. W., Thrush, B. A., and Wilkinson, J. P. T., paper presented at IMA Symposium on Ozone, Toronto, June, (1978)
- CODATA(1979). Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.
- Cox, R. A., and Derwent, R. G., "Kinetics of the Chlorine-Photosensitized Oxidation of Hydrogen at 1 Atmosphere Pressure, 306 K," J. Chem. Soc., Faraday Trans. 1 **73**, 272-283 (1977)
- Leu, W.-T., and DeMore, W. B., "Rate Constants at 205 K for the Reactions of Atomic Chlorine with H₂O₂, H₂O, O₃, CH₄ and H₂N₂," Chem Phys. Lett. **41**, 121-124 (1976)
- NASA RP-1010: "Chlorofluoromethanes and the Stratosphere" R. D. Hudson, Editor, August 1977 This reference contains the NASA (1977) rate constant recommendations.

NASA (1979). Recommendations of the NASA Panel for Data Evaluation, "published in NASA RP 1049 "The Stratosphere: Present and Future," V. D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the June 1979 Harpers Ferry Workshop).

Poulet, G., Le Bras, G., and Combourieu, J., "Kinetic Study of the Reactions of Cl Atoms with HNO_3 , N_2O_2 , and N_2 ," J. Chem. Phys. **55**, 767-773 (1978)

V. P. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No | Reaction/Reference | Temp. Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncert Factor at 298K, notes |
|---------|--|------------------|--|---------------------------------|
| 20,35Br | H ₂ + Br → HBr + O ₂ | | ΔH (298) = -151 kJ/mol | |
| | NASA (1979) eval | 200-300 | 2 × 10 ⁻¹¹ | 3 |
| | CMDATA (1979) eval | 298 | 1 × 10 ⁻¹¹ exp((0±250)/T) | 5 |

Changed from NASA 1010. Revised estimate of the rate constant, as there are still no experimental data. The rate constant for such an atom-radical process is expected to be rapid and relatively insensitive to temperature

REFERENCES

CMDATA(1979). Recommendations of the CMDATA Task Group on Chemical Kinetics to be published in the Journal of Physical and Chemical Reference Data.

NASA RP-1010. "Chlorofluoromethanes and the Stratosphere"
P. D. Hudson, Editor, August 1977 This reference contains the NASA (1977) rate constant recommendations.
NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future,"
P. D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the June 1979 Harpers Ferry Workshop).

P. F. Baepson
June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Reaction/Reference Temp. Reaction Rate Constant Uncert. Factor
Range/K $\text{h/cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298K, notes

| | | | | |
|-------|---|-----|--|-----|
| 20.36 | $\text{H}_2 + \text{Cl}_2 \rightarrow 2\text{HCl} + \text{H}_2$ | | $\Delta H (298) = -182 \text{ kJ/mol}$ | |
| | NASA (1979) eval | 298 | 5.2×10^{-12} | 1.5 |
| | COBATA (1979) eval | 298 | 5.2×10^{-12} | 1.5 |
| | Reisman, Kaufman (1978) | 298 | 3.8×10^{-12} | |
| | Howard, et al (1979) | 298 | 6.0×10^{-12} | |
| | Birks, Leck (1979) | 298 | 5.7×10^{-12} | |

The preferred value at 298 K was obtained by taking a simple mean of the results reported by Howard et al (private communication, 1979); Birks and Leck (private communication, 1979); and Reisman and Kaufman (1978). No recommendation is given for the temperature dependence of this reaction. Howard et al have reported that the reaction exhibits nonlinear Arrhenius behavior, with the rate constant increasing as temperature decreases. The magnitude of the temperature dependence below 300 K is similar to that reported by Cox (1978) for $\text{H}_2 + \text{H}_2$.

REFERENCES

COBATA (1979). Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.

Cox, R. A., 1978a, Paper presented at WMO Symposium on Ozone, Toronto, June, (1978)

NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA EP 1049 "The Stratosphere: Present and Future," R. D. Hudson and R. L. Reid, Editors, Dec. 1979 (report of the June 1979 Harpers Ferry Workshop).

Reisman, R., and Kaufman, R., "Rate Constant of the Reaction $\text{H}_2 + \text{Cl}_2 \rightarrow 2\text{HCl} + \text{H}_2$," J. Chem Phys. 52, 2925-2926 (1970)

R. P. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Temp. Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncertainty Factor at 298K, notes |
|---------|--|------------------|--|--------------------------------------|
| 20.36Br | NO ₂ + BrO → NO ₂ + O ₂ | | ΔH (298) = -207 kJ/mol | |
| | NASA (1979) eval | 298 | 5 × 10 ⁻¹² | 5 |
| | CODATA (1979) eval | 256 | 5 × 10 ⁻¹² | 3 |

No data; value chosen to be consistent with k(NO₂ + ClO)

REFERENCES

CODATA(1979). Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.

NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA SP 1049 "The Stratosphere: Present and Future," B. D. Hudson and E. L. Reed, Editors, Dec. 1975 (report of the June 1975 Harper Ferry Workshop).

B. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL

Reaction Rate Constant
 $\text{l}/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$

2

| 20.45 | $\text{H}_2 + \text{C}_2 - \text{C}_2 + \text{H}$ | 300 | -10^{-19} | $\Delta W (298) = -246 \text{ kJ/mol}$ | a |
|-------|---|----------|---|--|------|
| | ethic survey | 700-1000 | $2.5 \times 10^{-10} \exp(-11900/T)$ | | b |
| | Baulch, et al (1976) review | 300-1000 | $1.7 \times 10^{-13} \exp(-5000/T)$ | | c, d |
| | Lloyd (1974) eval | 300 | -1×10^{-12} | | e |
| | Westenberg, deHaas (1972a) | 300 | -10^{-20} | | e |
| | Davis, Payne, Stief (1973) | 300 | -3×10^{-18} | | e |
| | Wysocki, et al (1974) | 373-473 | -5×10^{-18} | | f |
| | Simonaitis, Heicklen (1973a) | 330 | -10^{-15} | | e |
| | Volman, Gorse (1972) | 713-773 | $1 \times 10^{-10} \exp(-11500/T)$ | | |
| | Belwin, Walker, Webster (1970) | | | | |
| | Vardanyan, Danyan, | | | | |
| | Sachyan (1972) | 678-952 | $2.2 \times 10^{-10} \exp(-11500/T)$ | | |
| | | | a. Review of all data listed here. | | |
| | | | b. Based on Davis, Payne and Stief (1972) and high + results. Temperature coef probably maximum value. | | |
| | | | c. Indirect measurement using a low-pressure discharge flow system. | | |
| | | | d. Relative rate measurement - reference reaction: $\text{H} + \text{H}_2 \rightarrow \text{H} + \text{H}_2$ | | |
| | | | e. Relative rate measurement - reference reaction: $\text{H}_2 + \text{H}_2 \rightarrow \text{H}_2 + \text{H}_2$ | | |
| | | | f. Relative rate measurement - reference reaction: $\text{H} + \text{C}_2 \rightarrow \text{C}_2 + \text{H}$ | | |

Upper limit only. The low value of k selected in this evaluation is based on the evaluation by Lloyd and the measurements by Davis, Payne, Stief and Simonaitis. Heicklen

REFERENCES

- Baldwin, F. P., Walker, R. W., and Webster, S. J., "The Carbon Monoxide-Sensitized Decomposition of Hydrogen Peroxide," *Combust. Flame* **15**, 167-172 (1970)
- Beulch, D. L., Drysdale, D. D., Duxbury, J., and Grant, S. J., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 3: Homogeneous Gas Phase Reactions of the O_2-O_3 System, the CH_4-H_2 System, and of Sulphur-Containing Species," (Butterworths, London, 1976)

- Davis, D. D., Payne, W., and Stief, L., "The Hydroperoxyl Radical in Atmospheric Chemical Dynamics: Reaction with Carbon Monoxide," *Science* **179**, 280-282 (1973)
- Lloyd, A. C., "Evaluated and Estimated Kinetic Data for Gas Phase Reactions of the Hydroperoxyl Radical," *Int. J. Chem. Kinet.* **6**, 169-228 (1974)
Supersedes NBS Report 10447
- Simenaltis, R., and Heicklen, J., "The Reactions of H_2 with Carbon Monoxide and Nitric Oxide and the Reaction of $d(1D)$ with Water," *J. Phys. Chem.* **77**, 1096-1102 (1973a)
- Steinberg, A. A., and deHaas, N., "Steady-State Intermediate Concentrations and Rate Constants, Some H_2 Results," *J. Phys. Chem.* **76**, 1586-1593 (1972a)
- Vyatch, D., Wendt, R. E., and Kunziker, R. E., "Modulation Kinetic Spectroscopy of $H_2/H_2/O_2$ Mixtures: Reactions of H_2 and H_2O_2 ," *XI, Int. Symp. on Free Radicals (Berchtesgaden-Konferenz, Sept. 4-7, 1973)* Paper No. 36; see also, *Ber. Bunsenges. Physik. Chem.* **78**, 204 (1974)
- Verdanyan, I. A., Danayan, T. M., and Sachyan, G. A., "Rate Constants for the Reaction $H_2 + CO \rightarrow CO_2 + OH$," *Dokl. Phys. Chem.* **205**, 632-634 (1972); *Tr. of Dokl. Akad. Nauk SSSR* **205**, 619-621 (1972)
- Volman, D. H., and Gorse, R. A., "Rate Constant for the Reaction of H_2 with Carbon Monoxide," *J. Phys. Chem.* **76**, 3301-3302 (1972)

R. F. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No | Reaction/Reference | Temp Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncert Factor at 298K, notes |
|-------|--|-----------------|--|---------------------------------|
| | | | | |
| 20.48 | H ₂ + CH ₂ ^o - H ₂ ^o + CH ₂ allroyd (1974) review | 300-600 | ΔH (298) = 8 kJ/mol 1.7 x 10 ⁻¹² exp (-4000/T) | >10 at 300K, 1.5 at 800K |
| | Baldwin, et al (1972) | 773 | 1.6 x 10 ⁻¹⁵ (a) Derived by computer fit to data | (a) |

This evaluation accepts the recommendation in Lloyd's (1974) review. Note the large error limits at room temperature

REFERENCES

- Baldwin, B. R., Fuller, A. R., Longthorn, D., and Walker, R. W., "Addition of Formaldehyde to Slowly Reacting Hydrogen + Oxygen Mixtures," J. Chem. Soc., Faraday Trans. I 68, 1362-1367 (1972)
- Lloyd, A. C., "Evaluated and Estimated Kinetic Data for Gas Phase Reactions of the Hydroperoxyl Radical," Int. J. Chem. Kinet, 6, 169-228 (1974)
Supersedes NBS Report 1047

B. F. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No | Reaction/Reference | Temp | | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncert Factor at 298K, notes |
|-------|--|---------|-------------------------------------|--|---------------------------------|
| | | Range/K | | | |
| 20.51 | NO ₂ + CH ₃ O ₂ → CH ₃ O ₂ H + O ₂ | | ΔH (298) = -140 kJ/mol | | |
| | NASA (1979) eval | 298 | 6 × 10 ⁻¹² | | 3 |
| | CEDATA (1979) eval | 298 | 6.5 × 10 ⁻¹² | | 2 |
| | Cox, Tyndall (1979) | 274-338 | 7.7 × 10 ⁻¹⁴ exp(1296/T) | | |

The room temperature value is that of Cox and Tyndall (1979). This study also reports a large negative E/R value over the temperature range 274-338K. This is similar to that found by this group for HO₂ + H₂. This requires independent verification. No recommendations for A or E/R are suggested at the present time.

REFERENCES

- CEDATA(1979) Recommendations of the CEDATA Task Group on Chemical Kinetics To be published in the Journal of Physical and Chemical Reference Data.
- Cox, R. A., and Tyndall, G. S., "Rate Constants for Reactions of CH₃O₂ in the Gas Phase," Chem. Phys. Lett. 55, 357-360 (1979)
- NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future."
- R. D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the June 1975 Harpers Ferry Workshop).

R. F. Ramsdon
June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS
Reaction/Reference

Uncert Factor
at 298K, notes

Temp.
Range/K

Reaction/Reference

No

Reaction Rate Constant
k/cm³molecule⁻¹s⁻¹

| | | | | |
|---------------------------------|--|-----|--|---------|
| 2 ^o , 5 ^o | H ₂ + C ₂ H ₄ → C ₂ H ₆ + H ₂ ? Walker (1973) | 773 | ΔH (298) = - 68 kJ/mol 2.5 x 10 ⁻¹⁷ (a) Relative to k (H ₂ + HCHO) = 1.6 x 10 ⁻¹⁵ | (a) |
| 2 ^o , 5 ^o | H ₂ + C ₂ H ₄ → addition products Lloyd (1974) review | 300 | -1.7 x 10 ⁻¹⁷ (a) Suggestion: Data are irreconcilable. | >10 (a) |

No recommendation

REFERENCES

- Lloyd, A. C., "Evaluated and Estimated Kinetic Data for Gas Phase Reactions of the Hydroperoxyl Radical," Int. J. Chem. Kinet. **6**, 169-228 (1974)
 Supersedes NBS Report 10447
- Walker, P. W., Comments on "Gas-Phase Oxidation of Butene-2: The Role of Acetaldehyde in the Reaction," by Ray, D. J., M., Diaz, P., R., and Washington, D. J., Symp. Combust. 14th (Combustion Institute, Pittsburgh, 1973) 265-266

R. F. Hampson
 May 1978

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Uncert Factor
at 298K, notes

Reaction/Reference

Temp
Range/K

Reaction Rate Constant
k/cm³molecule⁻¹s⁻¹

No

20.58 $\text{H}_2 + \text{C}_2\text{H}_6 \rightarrow \text{H}_2 + \text{C}_2\text{H}_5$

Lloyd (1974) review

300-1000

$\Delta H (298) = 53 \text{ kJ/mol}$

$-1.7 \times 10^{-12} \exp(-7000/T)$

(a) Relative rate data versus $2\text{H}_2 \rightarrow \text{H}_2 + \text{H}_2$ and $\text{H}_2 + \text{C}_6 \rightarrow \text{H}_2 + \text{C}_6$; Temp. coef. estimated.

10 (a)

No recommendation

REFERENCES

Lloyd, A. G. "Evaluated and Estimated Kinetic Data for Gas Phase Reactions of the Hydroperoxyl Radical," Int. J. Chem. Kinet. 6, 169-228 (1974)
Supersedes NBS Report 10447

R. F. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No | Reaction/Reference | Temp | | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncert Factor at 298K, notes |
|-------|---|----------|--|--|---------------------------------|
| | | Range/K | | | |
| 20,60 | H ₂ + C ₃ H ₆ → H ₂ O ₂ + 1-C ₃ H ₇ Lloyd (1974) review | 300-1000 | ΔH (298) = 39 kJ/mol 3.3 x 10 ⁻¹³ exp(-5300/T) (a) Based on upper limit meas. Temp coef estimated, | | 10 (a) |

No recommendation

REFERENCES

Lloyd, A. C., "Evaluated and Estimated Kinetic Data for Gas Phase Reactions of the Hydroperoxyl Radical," Int. J. Chem. Kinet. **6**, 169-228 (1974)
Supersedes NBS Report 10447

V. F. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS
Reaction/Reference Temp Reaction Rate Constant
Range/K $\text{K/cm}^3 \text{molecule}^{-1} \text{s}^{-1}$

Uncert Factor
at 298K, notes

No

| | | | |
|-------|---|---|--------|
| 20.0° | $\text{H}_2 + \text{m-C}_4\text{H}_9 \rightarrow \text{H}_2\text{D}_2 + \text{m-C}_4\text{H}_9$ | AN (298) = 45 kJ/mol | |
| | Lloyd (1974) review | $2.3 \times 10^{-13} \exp(-5300/T)$ | 10 (a) |
| | | (a) Based on upper limit meas, Temp coef estimated. | |

No recommendation

REFERENCES

Lloyd, A. C., "Evaluated and Estimated Kinetic Data for Gas Phase Reactions of the Hydroperoxyl Radical," Int. J. Chem. Kinet. 6, 169-228 (1974)
Supersedes NBS Report 10447

P. F. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No | Reaction/Reference | Temp Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncert Factor at 298K, notes | |
|-------|--|-----------------|---|---------------------------------|-----|
| | | | | | |
| 20,60 | H ₂ + 1-C ₄ H ₁₀ → W ₂ O ₂ + t-C ₄ H ₉ Lloyd (1974) review | 300-1000 | ΔH (298) = 32 kJ/mol 1.7 x 10 ⁻¹³ exp(-3500/T) (a) Based on upper limit meas; Temp: coef estimated. | 10 | (a) |

No recommendation

REFERENCES

Lloyd, A. C., "Evaluated and Estimated Kinetic Data for Gas Phase Reactions of the Hydroperoxyl Radical," Int. J. Chem. Kinet. 6, 169-228 (1974)
Supersedes NBS Report 10447

R. F. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Reaction/Reference
Temp
Range/K
Reaction Rate Constant
k/cm³molecule⁻¹s⁻¹
Uncert Factor
at 298K, notes

| | | | | |
|-------|---|---------|---|--|
| 20,60 | NO ₂ + alkane → H ₂ O ₂ + alkyl radical Walker (1977) | 300-500 | $k = 8 \times 10^{-14} [N_p \exp(-7520/T) + N_s \exp(-6330/T) + N_t \exp(-4990/T)]$ where N_p , N_s , and N_t are the number of primary, secondary, and tertiary hydrogen atoms respectively | |
|-------|---|---------|---|--|

This additivity rule can be used to estimate the rate constant for the overall rate of hydrogen atom abstraction from an alkane by the hydroperoxyl radical when there are no experimental data.

REFERENCES

Walker, R. E., "Rate Constants for Reactions in Gas-Phase Hydrocarbon Oxidation," Chapter 7 in "Gas Kinetics and Energy Transfer - Volume 2" A Specialist Periodical Report, The Chemical Society, London (1977)

R. F. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No | Reaction/Reference | Temp. Range/K | Reaction Rate Constant $k/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$ | Uncert Factor at 298K, notes |
|-------|--|------------------|--|---------------------------------|
| 21.35 | $\text{H}_2 + \text{Cl} \rightarrow \text{HCl} + \text{H}$ (1) | | $\Delta H(298) = 4 \text{ kJ/mol}$ | |
| 18.39 | $\text{H} + \text{HCl} \rightarrow \text{H}_2 + \text{Cl}$ (r) | | | |
| | NASA (1979) eval | 200-300 | $k_f = 3.5 \times 10^{-11} \exp(-(2290 \pm 200)/T)$ | 1.5 |
| | CODATA (1979) eval | 210-1070 | $k_f = 4.7 \times 10^{-11} \exp(-(2340 \pm 200)/T)$ | 1.5 |
| | Watson (1977) eval | 200-300 | $k_f = 3.5 \times 10^{-11} \exp(-2290/T)$ | |
| | Watson, et al (1975) | 213-350 | $k_f = (5.5 \pm 0.5) \times 10^{-11} \exp(-2375 \pm 100/T)$ | |
| | Lee, et al (1977) | 200-500 | $k_f = (2.66 \pm 0.42) \times 10^{-11} \exp(-2230 \pm 60/T)$ | |
| | Ambidge, et al (1976a) | 298-521 | $k_r = 7.8 \times 10^{-12} \exp(-1600 \pm 84/T)$ | |
| | Spencer, Glass (1975) | 295 | $k_r = 4.3 \times 10^{-14}$ | |

Unchanged from NASA 1010. This value is based on the results obtained below 300 K by Watson et al (1975) and Lee et al (1977). Although the results of these two studies are in agreement below 300 K, the data at higher temperatures are in somewhat poorer agreement. Further, the combined expression, when combined with relative rate data for the reaction of atomic chlorine with H_2 and CH_4 , gives rates for $\text{Cl} + \text{CH}_4$ at 300 K and above which are significantly lower than those measured directly. The combined expression also is in poor agreement with the high temperature measurements of $k(\text{Cl} + \text{H}_2)$ by Benson et al (1969). Thus, although this reaction is not important in the stratosphere, additional studies are needed particularly in the temperature region above 300 K.

REFERENCES

- Ambidge, P. F., Bradley, J. N., and Whytock, D. A., "Kinetic Study of the Reaction of Hydrogen Atoms with Hydrogen Chloride," J. Chem. Soc. Faraday Trans. 1 **72**, 2143-2149 (1976a)
- CODATA(1979). Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.

- Lee, J. E., Michael, J. V., Payne, W. A., Stief, L. J., and Phytocck, D. A., "Absolute Rate of the Reaction of $\text{Cl}(^2\text{P})$ with Molecular Hydrogen from 200-500 K.," J. Chem. Soc., Faraday Trans. 1 **73**, 1530-1536 (1977)
- NASA SP-1010, "Chlorofluoromethanes and the Stratosphere"
- R. D. Hudson, Editor, August 1977 This reference contains the NASA (1977) rate constant recommendations.
- NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," R. D. Hudson and E. L. Reed, Editors, Dec. 1979 (report of the June 1979 Harpers Ferry Workshop).
- Spencer, J. E. and Glass, G. P., "A Reexamination of the Reaction $\text{H} + \text{HCl} \rightarrow \text{H}_2 + \text{Cl}$," J. Phys. Chem. **79**, 2329-2335 (1975)
- Watson, R. T., "Rate Constants for Reactions of Cl^4 of Atmospheric Interest," J. Phys. Chem. Ref. Data **6**, 871-916 (1977)
- Watson, R. T., Machado, E. S., Schiff, E. L., Fischer, S., and Davis, D. B., 1975, Proceedings of the 4th CIAA Conference. D61-ISC-651-75-38. Cambridge, Mass., February 1975; also manuscript in preparation.
- R. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Temp. Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncertainty Factor at 298K, notes |
|--------|------------------------------|------------------|--|--------------------------------------|
| 21,38F | $H_2 + F \rightarrow HF + H$ | | $\Delta H(298) = -135 \text{ kJ/mol}$ | |
| | NASA (1979) eval | 200-300 | $2.6 \times 10^{-10} \exp(-(620 \pm 250)/T)$ | 1.5 |
| | CORATA (1979) eval | 200-400 | $2.6 \times 10^{-10} \exp(-(620 \pm 250)/T)$ | 1.5 |
| | Bennett, et al (1970) | 258-400 | $2.66 \times 10^{-10} \exp(-805/T)$ | |
| | Dodenov, et al (1971) | 293 | 3×10^{-11} | |
| | Clyne, et al (1973) | 258 | 2.8×10^{-11} | |
| | Bozzelli (1973) | 257 | 2.8×10^{-11} | |
| | Igoshin, et al (1974) | 155-296 | $1.55 \times 10^{-10} \exp(-544/T)$ | |
| | Kemp, Wanner (1972) | 258 | 6.3×10^{-11} | |
| | Habideau, et al (1972) | 293 | 6.6×10^{-12} | |
| | Ian, et al (1974) | 300 | 2.3×10^{-12} | |

New entry. The value of k at ~298 K seems to be fairly well established with the results of Bennett et al (1970), Dodenov et al (1971), Clyne et al (1973), Bozzelli (1973), and Igoshin et al (1974) being in excellent agreement considering the diverse nature of the experimental techniques used. The value reported by Kemp and Wanner (1972) appears to be too high by a factor of ~2.5, whereas the values reported by Habideau et al (1972) and Ian et al (1974) are too low by factors of 4 and 10, respectively. Therefore, the preferred value at 298 K is taken to be a mean of the five studies which are in good agreement. However, the magnitude of the temperature dependence cannot be considered to be well established with values of E/E of 805 (Bennett et al) and 544 (Igoshin et al) being reported. The preferred Arrhenius parameters were derived by calculating A to be 2×10^{-10} and calculating an E/E value to yield a value of 2.5×10^{-11} at 298 K. For detailed comments refer to reviews by Jones and Sholnik (1976) and Foon and Kaufman (1975). A-factor seems high.

REFERENCES

- Bozzelli, J. W., "Kinetics and Mechanism of the Reactions of Atomic Fluorine with Several Perhalomethanes and Hydrogen," *Trans. Am. Chem. Soc.*, **54**, 608-609 (1972)
- Clyne, M. A., A. A. McKenney, D. J., and Walker, R. F., "Reaction Kinetics of Ground State Fluorine, F(²P), Atoms. I. Measurement of Fluorine Atom Concentrations and the Rates of Reactions F + CHF₃ and F + Cl₂ using Mass Spectrometry," *Can. J. Chem.*, **51**, 3596-3604 (1973)

CODATA(1979). Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.

Bedelev, A. P., Lavrenko, G. K., Morozov, I. I., and Ial'roze, V. I., "Mass Spectrometric Determination of the Rate Constant for the Elementary Reaction of Fluorine Atoms with Hydrogen," Dokl. Phys. Chem. **193**, 446-448, (1971) tr. of Dokl. Akad. Nauk SSSR **193**, 622-625 (1971)

Feen, B., and Kaufman, M., "Kinetics of Gaseous Fluorine Reactions," Progress in Reaction Kinetics, **5**, 81 (1975)

Bonann, L. B., Seligson, W. C., Barnatz, J., Wagner, E. G., and Zetzsch, C., "Eine Methode zur Erzeugung von Fluoratomen in Inertem Atmosphäre," Ber. Bunsenges. Phys. Chem. **74**, 868-885 (1976)

Igenbin, V. I., Bulskov, I. V., and Nimitin, A. I., "Determination of the Rate Constant of the Chemical Reaction $F + H_2 (D_2) \rightarrow HF(DF) + H(D)$ from the Stimulated Emission of the $HF(DF)$ Molecules," Sov. J. Quant. Electron., **3**, 266-311 (1974) tr. of Invent. Elec. **3**, 1-144 (1973)

Jones, W. E., and Skolnik, E. G., "Reactions of Fluorine Atoms," Chem. Rev. **76**, 563-892 (1976)

Koupe, L. I., and Vanner, J., "Study of Some Fluorine Atom Reactions using a Chemical Laser Method," Chem. Phys. Lett. **12**, 560-563 (1972)

Las Thau, M., Pegon, M., and Puget, P., "Etude Cinétique du Laser Chimique HF Continu Produit Par la Réaction des Atomes de Fluor Avec $L'H_2$ et $L'D_2$ et Quelques Aléances," J. De. Chimie Physique, **71**, 377-382 (1974)

NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA SP 1049 "The Stratosphere: Present and Future," E. B. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the June 1979 Harpers Ferry Workshop).

Rebideau, G. W., Hecht, E. G., and Lewis, W. E., "A Study of the Kinetics of the Reaction Between H_2 and F_2 by EPR Methods," J. Magn. Reson. **5**, 384-395 (1972)

E. F. Baer
June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Reaction/Reference Temp. Reaction Rate Constant
Range/K k/cm³molecule⁻¹s⁻¹

Uncert Factor
at 298K, notes

21.36 H₂ + ClO → products
NASA (1979) eval

200-300 $\pm 1 \times 10^{-12}$ exp(-4800/T)
298 $\pm 1 \times 10^{-19}$

Unchanged from NASA 1010. These upper limits are based on the data of Walker (reported in Clyne and Watson (1974a))
The upper limits shown for k (298) were estimated from data collected at either 587 K or 670 K. The Arrhenius
expressions were estimated based on this ~ 600 K data by choosing the "A factor".

REFERENCES

- Clyne, M. A. L., and Watson, R. To. "Kinetic Studies of
Diatomic Free Radicals using Mass Spectrometry Part 2.
Rapid Bimolecular Reactions Involving the ClO X²Π Radical,"
J. Chem. Soc., Faraday Trans. 1 70, 2250-2259 (1974a)
- NASA RP-1010: "Chlorofluoromethanes and the Stratosphere"
R. D. Hudson, Editor, August 1977 This reference contains
the NASA (1977) rate constant recommendations.
NASA (1979). Recommendations of the NASA Panel for Data Evaluation,
published in NASA RP 1049 "The Stratosphere: Present and Future,"
R. D. Hudson and E. L. Reed, Editors, Dec. 1979 (report of the
June 1979 Harpers Ferry Workshop).

R. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Reaction/Reference
 Temp.
 Range/T
 Reaction Rate Constant
 $k/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$
 Uncert Factor
 at 298K, notes

No

22, 29 $\text{H}_2\text{O} + \text{SO}_3 \rightarrow \text{products}$
 CODATA (1979) eval
 Castleman, et al (1975)

298
 No recommendation
 (9.182-9) $\times 10^{-13}$

This is the only reported study - no recommendation

REFERENCES

Castleman, A. W., Jr., Davis, R. E., Munkelwitz, H. E., Tang, I. M., and
 Wood, W. P., "Kinetics of Association Reactions Pertaining to H_2SO_4
 Aerosol Formation," Int J Chem Kinet, Symp. No. 1, 629-640 (1975)

CODATA(1979), Recommendations of the CODATA Task Group on Chemical
 Kinetics. To be published in the Journal of Physical and Chemical
 Reference Data.

R. F. Hampson
 June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Temp. Range/K | Reaction Rate Constant k/cm ³ -molecule ⁻¹ s ⁻¹ | Uncert. Factor at 250K, notes |
|--------|-------------------------------|------------------|---|----------------------------------|
| 22.35P | H ₂ O + F → HF + H | | | |
| | NASA (1979) eval | 200-300 | $2.2 \times 10^{-11} \exp(-200 \pm 200/T)$ | 5 |
| | CODATA (1979) eval | 240-360 | $2.2 \times 10^{-11} \exp(-200 \pm 200/T)$ | 3 |
| | Zetzsch (1971) | 243-365 | $2.2 \times 10^{-11} \exp(-201/T)$ | |

This is the value of Zetzsch (1971) which was reported in the review of Jones and Shelnik (1976). The reactivity appears to be somewhat lower than might be expected for such a hydrogen abstraction reaction (see review of Foon and Kaufman (1975))

REFERENCES

CODATA(1979). Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.

Foon, R., and Kaufman, M., "Kinetics of Gaseous Fluorine Reactions," Progress in Reaction Kinetics, **8**, 21 (1975)

Jones, W. R., and Shelnik, E. G., "Reactions of Fluorine Atoms," Chem. Rev. **76**, 563-592 (1976)

NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," E. D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the June 1975 Harpers Ferry Workshop).

Zetzsch, C., 1971, Ph.D. dissertation, Georg-August University, Göttingen.

R. F. Simpson
 June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No | Reaction/Reference | Temp Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncert Factor at 298K, notes |
|--------|--|-----------------|--|---------------------------------|
| 23, 35 | H ₂ O ₂ + Cl - HCl + HO ₂ | | ΔH (298) = - 75 kJ/mol | |
| | NASA (1979) eval | 200-300 | 1.1 x 10 ⁻¹¹ exp(-(980±500)/T) | 1.5 |
| | CBDATA (1979) eval | 265-424 | 1.0 x 10 ⁻¹¹ exp(-(980±500)/T) | 1.5 |
| | Keyser (1979) | 298-424 | (1.05±0.31) x 10 ⁻¹¹ exp(-(982±102)/T) | |
| | Michael, et al (1977) | 265-400 | (1.24±0.74) x 10 ⁻¹² exp(-(384±168)/T) | |
| | Poulet, et al (1978) | 298 | (4.0±0.4) x 10 ⁻¹³ | |
| | Leu, DeMore (1976) | 295 | (6.2±1.5) x 10 ⁻¹³ | |
| | Watson, et al (1976) | 298 | 5.2 x 10 ⁻¹³ | |

This revised value is based on the Arrhenius expression reported by Keyser (1979). The A-factor reported by Michael et al (1977) is considerably lower than that expected from theoretical considerations and may possibly be attributed to decomposition of H₂O₂ at temperatures above 300K. The data of Michael et al at and below 300K are in good agreement with the Arrhenius expression reported by Keyser. More data are required before the Arrhenius parameters can be considered to be well-established.

REFERENCES

- CBDATA(1979). Recommendations of the CBDATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.
- Keyser, L., Manuscript in preparation. Jet Propulsion Laboratory, Pasadena, CA. 91003 (1979)
- Leu, M-T., and DeMore, W. E., "Rate Constants at 295 K for the Reactions of Atomic Chlorine with H₂O₂, HO₂, O₃, CH₄ and HNO₃," Chem Phys Lett, **41**, 121-124 (1976)
- Michael, J. V., Whytock, D. A., Lee, J. E., Payne, W. A., and Stief, L. J., "Absolute Rate Constant for the Reaction of Atomic Chlorine with Hydrogen Peroxide Vapor over the Temperature Range 265-400 K," J. Chem. Phys. **67**, 3533-3536 (1977)
- NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA SP 1049 "The Stratosphere: Present and Future," W. D. Hudson and E. L. Reed, Editors, Dec. 1979 (report of the June 1979 Warners Ferry Workshop).

Poulet, G., Le Bras, G., and Combourieu, J., "Kinetic Study
of the Reactions of Cl Atoms with HNO_3 , H_2O_2 , and H_2O ,"
J. Chem. Phys. **62**, 767-773 (1978)
Watson, R., Machado, G., Fischer, S., and Davis, D. D., "A Temperature
Dependence Kinetics Study of the Reaction of $\text{Cl}(\text{ }^2\text{P}_{3/2})$ with O_3 , CH_4 , and
 H_2O_2 ," J. Chem. Phys. **65**, 2126-2138 (1976)

R. F. Hampson
June 1979

D

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No | Reaction/Reference | Temp | | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncert Factor at 298K, notes |
|---------|--|---------|--------------------------------------|--|---------------------------------|
| | | Range/K | | | |
| 23, 35B | H ₂ O ₂ + Br -> HBr + H ₂ O | | ΔH (298) = - 10 kJ/mol | | |
| | NASA (1979) eval | 200-300 | < 2 x 10 ⁻¹² exp(-1400/T) | | 2, 0-02 |
| | CMDATA (1979) eval | 298 | < 2 x 10 ⁻¹⁴ | | 2, 0-02 |
| | Leu, DeMore (1978) | 298 | < 2 x 10 ⁻¹⁴ | | |

Changed from NASA 1010. Alternative selection of Arrhenius parameters consistent with unpublished upper limit reported for k (298 K) by Leu and DeMore (1978a). No temperature dependent data available

REFERENCES

CMDATA(1979). Recommendations of the CMDATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.

Leu, V. T., and DeMore, W. B., 1978a, Provisional unpublished data. Jet Propulsion Laboratory.

NASA RP-1010. "Chlorofluoromethanes and the Stratosphere"

R. D. Hudson, Editor, August 1977 This reference contains the NASA (1977) rate constant recommendations.

NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," R. D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the June 1979 Harpers Ferry Workshop).

P. F. Hampson
 June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No | Reaction/Reference | Temp Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncert Factor at 298K, notes |
|--------|---|-----------------|--|---------------------------------|
| | | | | |
| 24, 24 | ENG • ENG - H ₂ O • N ₂ O | | ΔH (298) = -359 kJ/mol | |
| | •Baulch, et al (1973) review | 300 | 4 x 10 ⁻¹⁵ | 2 |

This evaluation accepts the recommendation in the review of Baulch et al (1973)

REFERENCES

Baulch, D. L., Drysdale, D. D., and Horne, D. G., "Evaluated Kinetic Data for Fish Temperature Reactions, Vol. 2: Homogeneous Gas Phase Reactions of the H₂-N₂-O₂ System," (Butterworths, London, 1973)

P. F. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Uncert Factor
at 298K, notes

| No | Reaction/Reference | Temp Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | |
|-------|--|-----------------|--|----------|
| | | | AR (298) = - 8 kJ/mol | |
| 26.35 | PN ₃ + Cl -> PCl + N ₂ | | | |
| | NASA (1979) eval | 200-300 | $\pm 1 \times 10^{-11} \exp(-2170/T)$ $A(E/R) = +2500, -500$ $\pm 7 \times 10^{-15}$ | 2, 0-003 |
| | CODATA (1979) eval | 298 | $(6.8 \pm 3.4) \times 10^{-15}$ | 2, 0-003 |
| | Leu, DeMore (1976) | 295 | | |
| | Poulet, et al (1978) | 439-633 | $1.5 \times 10^{-11} \exp(-4380/T)$ | |
| | | 298 | $\pm 2 \times 10^{-17}$ | |

Unchanged from NASA 1010. Neither study (Leu and DeMore (1976), and Poulet et al (1978)) can be considered to be definitive. Poulet et al postulated that Leu and DeMore were observing removal of HNO₃ via a heterogeneous process while this hypothesis is certainly tenable, the value of E/R reported by Poulet et al is much higher than would be expected (resulting in a surprisingly low value for k at 298 K). Although this reaction is not important in atmospheric chemistry, additional studies are required to provide accurate Arrhenius parameters. Until further data becomes available the preferred value is based on assuming that the data of Leu and DeMore represents an upper limit. The uncertainties in k (298 K) and E/R allow for the data of Poulet et al to be correct

REFERENCES

- CODATA(1979). Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.
- Leu, M-T., and DeMore, W. B., "Rate Constants at 295 K for the Reactions of Atomic Chlorine with H₂, H₂O, O₃, CH₄, and HNO₃," Chem Phys. Lett, **41**, 121-124 (1976)
- NASA PP-1010: "Chlorofluoromethanes and the Stratosphere"
R. D. Hudson, Editor, August 1977 This reference contains the NASA (1977) rate constant recommendations.

NASA (1979). Recommendations of the NASA Panel for Data Evaluation,
published in NASA PP 1049 "The Stratosphere: Present and Future,"
E. D. Hudson and E. L. Reed, Editors, Dec. 1979 (report of the
June 1979 Harpers Ferry Workshop);
Poulet, G., Le Bras, G., and Combarieu, J., "Kinetic Study
of the Reactions of Cl Atoms with HNO_3 , H_2O_2 , and H_2 ,"
J. Chem. Phys. 69, 767-773 (1978)
P. F. Haysom
June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No | Reaction/Reference | Temp. Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncert. Factor at 298K, notes |
|----------|---|------------------|--|----------------------------------|
| | | | | |
| 26a, 34b | S + CS ₂ → S ₂ + CS | | ΔH (298) = 6 kJ/mol | |
| | Baulch, et al (1976) review | 298 | 6.5 x 10 ⁻¹³ | 1.5 |

This evaluation accepts the recommendation in the review of Baulch et al (1976)

REFERENCES

Baulch, D. L., Drysdale, D. D., Duxbury, J., and Grant, S. J., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 3: Homogeneous Gas Phase Reactions of the C₂-C₃ System, the C₆-C₂-H₂ System, and of Sulphur-Containing Species," (Butterworths, London, 1976)

P. F. Hampson
May 1976

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Uncert Factor
at 298K, notes

Reaction/Reference
Temp.
Range/K
Reaction Rate Constant
k/cm³molecule⁻¹s⁻¹

No

26a.34c S + COS → CS + S₂ ΔH (298) = -117 kJ/mol
 Baulch, et al (1976) review 230-2600 2.8 x 10⁻¹² exp(-2050/T)

3

This evaluation accepts the recommendation in the review of Baulch et al (1976)

REFERENCES

Baulch, D. L., Drysdale, D. D., Duxbury, J., and Grant, S. J., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 3: Homogeneous Gas Phase Reactions of the C₂-C₃ System, the C₄-C₂-H₂ System, and of Sulphur-Containing Species," (Butterworths, London, 1976)

R. F. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Reaction/Reference Temp Range/K Reaction Rate Constant
k/cm³molecule⁻¹s⁻¹

Uncert Factor
at 298K, notes

| | | | | | |
|-------|---|------|--|-------------------------------|--|
| 27.27 | SO + SO ₂ → S or (SO) ₂ | | | ΔH (298) = - 30 kJ/mol | |
| | Schofield (1973) review | 300 | | < 3 x 10 ⁻¹⁵ | |
| | | 1000 | | < 2 x 10 ⁻¹³ | |
| | Chung, Calvert, Bottenheim (1975) | 300 | | 8.3 ± 6.7 x 10 ⁻¹⁶ | |

No recommendation

REFERENCES

- Chung, K., Calvert, J. G., and Bottenheim, J. W., "The Photochemistry of Sulfur Dioxide Excited within its First Allowed Band (3130 Å) and the 'Forbidden' Band (3700-4000 Å)," Int. J. Chem. Kinet. **7**, 161-182 (1975)
- Schofield, K., "Evaluated Chemical Kinetic Rate Constants for Various Gas Phase Reactions," J. Phys. Chem. Ref. Data **2**, 25-84 (1973)
- K. F. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS
Reaction/Reference Temp. Reaction Rate Constant
Range/K k/cm³molecule⁻¹s⁻¹

Uncert. Factor
at 298K, notes

No

27.29 $\text{SO} + \text{SO}_3 \rightarrow 2\text{SO}_2$ $\Delta H (298) = -203 \text{ kJ/mol}$
Chung, Calvert, Bottenheim (1975) 300 $2 \pm 1.2 \times 10^{-15}$

No recommendation

REFERENCES

Chung, K., Calvert, J. G., and Bottenheim, J. W., "The Photochemistry of Sulfur Dioxide Excited within its First Allowed Band (3130 Å) and the 'Forbidden' Band (3700-4000 Å)," Int. J. Chem. Kinet. 7, 161-182 (1975)

P. F. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Uncert Factor
at 298K, notes

Reaction/Reference Temp.
Range/K $k/cm^3 molecule^{-1} s^{-1}$

No

28,49H $SO_2 + CH_3 (^{\circ}M) \rightarrow CH_3SO_2 (^{\circ}M)$
James, et al (1973)

3 x 10⁻¹³

300

This rate constant was found to be independent of pressure over the range 50 to 200 torr Ar and N₂

REFERENCES

James, F. C., Kerr, J. A., and Simons, J. P., "A Direct Measurement of
the Rate of Reaction of the Methyl Radical with Sulphur Dioxide," J. Chem.
Soc. Faraday Trans. I 69, 2124-2129 (1973)

R. F. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Uncert Factor
at 298K, notes

Reaction/Reference
Temp
Range/K
Reaction Rate Constant
k/cm³molecule⁻¹s⁻¹

No

| | | | | |
|--------|--|-----|-------------------------|-----|
| 31, 31 | H ₂ + H ₂ - H ₂ S + S | 205 | ΔH (298) = - 36 kJ/mol | 1-5 |
| | Baulch, et al (1976) review | | 1.3 x 10 ⁻¹¹ | |

This evaluation accepts the recommendation in the review of Baulch et al (1976)

REFERENCES

Baulch, D. L., Drysdale, D. D., Duxbury, J., and Grant, S. J., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 3: Homogeneous Gas Phase Reactions of the O₂-O₃ System, the CO-CO₂-H₂ System, and of Sulphur-Containing Species," (Butterworths, London, 1976)

G. F. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Uncert Factor
at 298K, notes

Reaction/Reference Temp.
Range/K Reaction Rate Constant
k/cm³molecule⁻¹s⁻¹

No

| | | | |
|--------|-----------------------------------|--|-----|
| 35,354 | Cl + Cl + M → Cl ₂ + M | ΔH (298) = -243 kJ/mol | |
| | Watson (1977) review | 6.3 x 10 ⁻³⁴ exp(906/T) cm ⁶ molecule ⁻² s ⁻¹ , M = Ar | 1 3 |

This evaluation accepts the recommendation in Watson's (1977) review

REFERENCES

Watson, R. G., "Rate Constants for Reactions of ClO₂ of Atmospheric Interest," J. Phys. Chem. Ref. Data 6, 871-918 (1977)

R. F. Hampson
May 1978

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

CHEMICAL KINETICS DATA SURVEY

Reaction/Reference

Temp Range/K

Uncert Factor at 298K, notes

No

Reaction Rate Constant
k/cm³ molecule⁻¹ s⁻¹

35, 37 Cl + CCl₄ → 2Cl₂
NASA (1979) eval
Bemand, Clyne, Watson (1973)
ΔH (298) = - 14 kJ/mol
5.9 x 10⁻¹¹ exp((0±250)/T)
(5.9±0.9) x 10⁻¹¹
(a) Recommended in Watson's (1977) review

1-25
(a)

Unchanged from NASA 1010c Data reported by Bemand, Clyne and Watson (1973)

REFERENCES

Bemand, P. P., Clyne, W. A., and Watson, R. T., "Reactions of Chlorine Oxide Radicals. Part 4: Rate Constants for the Reaction Cl + CCl₄, Cl + CCl₄, H + CCl₄, NO + CCl₄ and C + CCl₄," J. Chem. Soc., Faraday Trans. 1 69, 1356-1374 (1973)

NASA RP-1010c "Chlorofluoromethanes and the Stratosphere"

P. D. Hudson, Editor, August 1977 This reference contains

the NASA (1977) rate constant recommendations.

NASA (1979): Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future,"

P. D. Hudson and E. L. Reed, Editors, Dec. 1970 (report of the June 1979 Harpers Ferry Workshop).

Watson, R. T., "Rate Constants for Reactions of ClO_x of Atmospheric Interest," J. Phys. Chem. Ref. Data 6, 871-918 (1977)

P. P. Bemand
June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Uncert Factor
at 298K, notes

| No | Reaction/Reference | Temp Range/K | Reaction Rate Constant $k/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$ | Uncert Factor at 298K, notes |
|-------|--|---------------------------|--|---------------------------------|
| 35,37 | $\text{Cl} + \text{ClO} - \text{Cl}_2 + \text{O}_2$ (a) - 2ClO (b) NASA (1979) eval | 200-300 200-300 297 | ΔH (298) = -210 kJ/mol - - - 6 kJ/mol $k_a = 1 \times 10^{-10} \exp((0.250)/T)$ $k_b = 5 \times 10^{-12} \exp((0.250)/T)$ $k_a = 9.8 \times 10^{-11}$ $k_b = 4.7 \times 10^{-12}$ | 3 3 |
| | Cox, et al (1979) | 298 | $k_a = 1.56 \times 10^{-10}$ $k_a/k_b = 108$ | |
| | Johnston, et al (1969) | 298 | $k_a/k_b = 15$ | |
| | Nicholas, Norrish (1968) | 298 | | |

Changed from NASA 1010 due to new data. Cox et al (1979) reported values for k_a and k_b which result in a ratio of ~ 20.9 for k_a/k_b . This compares with values previously reported for k_a/k_b of 108 (Johnston et al (1969)) and 15 (Nicholas and Norrish (1968)). The absolute values of k_a and k_b are dependent upon the choice of ΔH° (ClO). The preferred values are taken to be those reported by Cox et al. The previous NASA 1010 values were based on the data reported by Johnston et al for k_a (in good agreement with Cox et al), and the ratio of k_a/k_b reported by Nicholas and Norrish. The Arrhenius parameters are estimated

REFERENCES

- Cox, R. A., Derwent, R. G., Eggleston, A. E. J., and Reid, R. J., "Kinetics of Chlorine Oxide Radicals using Modulated Photolysis, Part 2: - ClO and ClO Radicals Kinetics in the Photolysis of $\text{Cl}_2 + \text{H}_2 + \text{N}_2$ Mixtures," J. Chem. Soc. Faraday Trans. 1 **75**, 1648-1666 (1979)
- Johnston, R. S., Morris, E. D., Jr., and Van den Bogarde, J., "Molecular Modulation Kinetic Spectrometry: ClO and ClO Radicals in the Photolysis of Chlorine in Oxygen," J. Amer. Chem. Soc. **91**, 7712-7727 (1969)
- NASA RP-1010: "Chlorofluoromethanes and the Stratosphere"
- v. D. Hudson, Editor, August 1977 "This reference contains the NASA (1977) rate constant recommendations."
- NASA (1979): Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," R. D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the June 1979 Harbers Ferry Workshop).

Nicholas, J. E., and Norrish, R. G. W., "Some Reactions in the Chlorine and
Oxygen System Studied by Flash Photolysis," Proc. Roy. Soc. (London) A 307,
391-397 (1968)
R. F. Hampson
June 1979

01

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Uncert Factor
at 298K, notes

Reaction/Reference
Temp
Range/K
Reaction Rate Constant
k/cm³molecule⁻¹s⁻¹

No

| | | |
|--------|--|-------------------------|
| 35,44a | Cl + Cl ₂ O → Cl ₂ + ClO | ΔH (298) = -101 kJ/mol |
| | Watson (1977) review | 6.8 × 10 ⁻¹³ |

This evaluation accepts the recommendation in Watson's (1977) review

REFERENCES

Watson, R. T., "Rate Constants for Reactions of ClO_x of Atmospheric Interest," J. Phys. Chem. Ref. Data 6, 871-918 (1977)

R. F. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| Reaction/Reference | Temp. Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncert. Factor at 298K, notes |
|--------------------|------------------|--|----------------------------------|
|--------------------|------------------|--|----------------------------------|

| | | | |
|--|---------|--|-----|
| 35.42 Cl + NOCl → NO + Cl ₂ | 200-300 | AH (298) = - 83 kJ/mol 3.0 x 10 ⁻¹¹ | 2 |
| NASA (1979) eval | | Δ(E/R) = -500, -250 (3.0 ± 0.5) x 10 ⁻¹¹ | |
| Clyne, Cruse (1972) | 298 | (a) Recommended in Watson's (1977) review | (a) |

Unchanged from NASA 1010. Value based on the data of Clyne and Cruse (1972). No reliable data on the temperature dependence

REFERENCES

Clyne, W. A. A., and Cruse, E. W., "Atomic Resonance Fluorescence Spectrometry for Rate Constants of Rapid Bimolecular Reactions, Part 1, Reactions of NO₂, Cl + ClNO, Br + ClNO," J. Chem. Soc., Faraday Trans. II 68, 1281-1299 (1972)

NASA PP-1010, "Chlorofluoromethanes and the Stratosphere"
R. D. Hudson, Editor, August 1977 This reference contains the NASA (1977) rate constant recommendations.
NASA (1979), Recommendations of the NASA Panel for Data Evaluation, published in NASA TP 1049 "The Stratosphere: Present and Future," R. D. Hudson and E. L. Reed, Editors, Dec. 1979 (report of the June 1979 Harpers Ferry Workshop).

Watson, R. T., "Rate Constants for Reactions of ClO_x of Atmospheric Interest," J. Phys. Chem. Ref. Data 6, 871-918 (1977)

R. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Uncert Factor
at 298K, notes

Reaction/Reference
Temp
Range/K
Reaction Rate Constant
k/cm³molecule⁻¹s⁻¹

No

| | | | |
|-------|---|-----|----------------------------|
| 35,43 | Cl + NO ₂ Cl → NO ₂ + Cl ₂ | 298 | ΔH (298) = -100 kJ/mol |
| | Watson (1977) review | | k >> 3 x 10 ⁻¹⁴ |

No recommendation - entry based on provisional, unpublished data

REFERENCES

Watson, R. T., "Rate Constants for Reactions of Cl₂ of Atmospheric Interest," J. Phys. Chem. Ref. Data 6, 871-918 (1977)

R. F. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No | Reaction/Reference | Temp. Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncert Factor at 298K, notes |
|--------|------------------------------------|------------------|--|---------------------------------|
| | | | | |
| 35,43a | Cl + NO ₂ Cl → products | | | |
| | NASA (1979) eval | 200-300 | $1.7 \times 10^{-12} \exp(-6074388/T)$ | 2 |
| | CODATA (1979) eval | 224-273 | $1.7 \times 10^{-12} \exp(-610400/T)$ | 2 |
| | Kurylo, Manning (1977) | 224-273 | $1.68 \times 10^{-12} \exp(-607/T)$ | |
| | Pavishankara, et al (1976) | 245 | $\sim 9 \times 10^{-14}$ | preliminary |

Unchanged from NASA 1910. Considering the experimental difficulties associated with handling ClNO₂, and the low precision of the data of Pavishankara et al (1976), the results are in fair agreement at 245 K. Therefore, the preferred value is taken to be that reported by Kurylo and Manning (1977). Neither study reported any information which could be used to identify products

REFERENCES

- CODATA(1979). Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.
- Kurylo, M. J., and Manning, W. G., "Flash Photolysis Resonance Fluorescence Investigation of the Reaction of Cl(2p) Atoms with ClNO₂," Chem. Phys. Lett. **48**, 274-283 (1977)
- NASA RP-1010, "Chlorofluoromethanes and the Stratosphere"
 R. D. Hudson, Editor, August 1977 This reference contains the NASA (1977) rate constant recommendations.
- NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future,"
 R. D. Hudson and E. L. Reed, Editors, Dec. 1979 (report of the June 1979 Warpers Ferry Workshop).
- Pavishankara, A. R., Smith, G., Tesi, G., and Davis, D. D., Presented at 12th Informal Conference on Photochemistry, National Bureau of Standards, Gaithersburg, MD June 1976

P. F. Hampson
 June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| Reo | Reaction/Reference | Temp. Range/K | Reaction Rate Constant $k/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$ | Uncerto. Factor at 298K, notes |
|-------|---|------------------|--|-----------------------------------|
| 35.42 | $\text{Cl} + \text{CH}_2\text{O} \rightarrow \text{HCl} + \text{HCC}$ | | $\Delta H (298) = -67 \text{ kJ/mol}$ | |
| | NASA (1979) eval | 200-300 | $9.2 \times 10^{-11} \exp(-68100/T)$ | 1.15 |
| | CODATA (1979) eval | 200-500 | $7.5 \times 10^{-11} \exp(-68100/T)$ | 1.15 |
| | Anderson, Kurylo (1975) | 223-323 | $1.09 \times 10^{-10} \exp(-131498/T)$ | |
| | Michael, et al (1979) | 200-500 | $(7.48 \pm 0.5) \times 10^{-11}$ | |

See entry. The results of the three studies (Michael et al (1979), Anderson and Kurylo (1975), Niki et al (1978)) are in good agreement at ~298 K. The preferred value at 298 K was obtained by combining the absolute values reported by Michael et al and Anderson and Kurylo (7.18×10^{-11}), with the value (7.4×10^{-11}) obtained by combining the ratio of $k(\text{H}_2\text{CO})/k(\text{C}_2\text{H}_6)$ reported by Niki et al (1.340 ± 1) with the preferred value of $5.7 \times 10^{-11} \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1}$ for $k(\text{C}_2\text{H}_6)$ at 298 K. The value of E/R was based on averaging the values of Michael et al and Anderson and Kurylo.

REFERENCES

- Anderson, P. Co. and Kurylo, M. J., "Rate Constant Measurements for the Reaction $\text{Cl} + \text{CH}_2\text{O} \rightarrow \text{HCl} + \text{HCC}$: Implications Regarding the Removal of Stratospheric Chlorine," *J. Phys. Chem.* **83**, 2055-2057 (1979)
- CODATA(1979). Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.
- Michael, J. V., Nava, D. F., Payne, W. A., and Stief, L. J., "Rate Constant for the Reaction of Atomic Chlorine with Formaldehyde from 200 to 500 K," *J. Chem. Phys.* **70**, 1147-1150 (1979)
- NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA SP 1049 "The Stratosphere: Present and Future," E. D. Hudson and E. L. Reed, Editors, Dec. 1975 (report of the June 1975 Harpers Ferry Workshop).

Miki, M., Maher, P. B., Breitenbach, L. P., and Savage, C. M.,
FTIR Studies of the Kinetics and Mechanism for the
Reaction of Cl Atoms with Formaldehyde," Chem. Phys. Lett.
57, 556-555 (1978)

P. B. Hansen
June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS
Reaction/Reference

Uncert Factor
at 298K, notes

| No | Temp Range/K | Reaction/Reference | Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncert Factor at 298K, notes |
|-------|-----------------|--|--|---------------------------------|
| 35,56 | | Cl + CH ₄ → HCl + CH ₃ | ΔH (298) = 7 kJ/mol | |
| | 200-300 | NASA (1979) eval | 9.5 x 10 ⁻¹² exp(-(1359±150)/T) | 1.15 |
| | 200-300 | CODATA (1979) eval | 9.9 x 10 ⁻¹² exp(-(1360±150)/T) | 1.15 |
| | 200-300 | Watson (1977) review | 7.3 x 10 ⁻¹² exp(-1260/T) | (a) |
| | 218-322 | Manning, Kurylo (1977) | (7.93 ± 1.53) x 10 ⁻¹² exp(-1273 ± 51/T) | (b) |
| | 218-401 | Watson, et al (1976) | (7.94 ± 2.7) x 10 ⁻¹² exp(-1260 ± 35/T) | |
| | 200-500 | Whytock, et al (1977) | 5.44 x 10 ⁻¹⁹ T ^{2.50} exp(-608/T) | |
| | 200-299 | | (6.51 ± 0.79) x 10 ⁻¹² exp(-1229 ± 27/T) | |
| | 200-590 | Zahniser, et al (1978) | 8.6 x 10 ⁻¹⁸ T ^{2.11} exp(-795/T) | |
| | 200-300 | | (8.2 ± 0.6) x 10 ⁻¹² exp(-1320 ± 20/T) | |
| | 208-423 | Lin, Leu, DeMore (1972) | (1.07±0.4) x 10 ⁻¹¹ exp(-(1410±120)/T) | |
| | 220-298 | Keyser (1978) | (7.4±2.0) x 10 ⁻¹² exp(-(1291±68)/T) | |
| | 258-423 | | (1.65±0.3) x 10 ⁻¹¹ exp(-(1530±68)/T) | |
| | 255-490 | Poulet, et al (1974) | (1.84±0.14) x 10 ⁻¹¹ exp(-(1410±100)/T) | |
| | 258 | Michael, Lee (1977) | (1.08±0.07) x 10 ⁻¹³ | |
| | 300 | Devie, et al (1970) | 1.5 ± 0.1 x 10 ⁻¹³ | |
| | 300-686 | Fettie, Knox (1964) | 4 x 10 ⁻¹¹ exp(-1930/T) | |
| | | Clyne, Walker (1973) | 5.1 x 10 ⁻¹¹ exp(-1790/T) | |
| | | | (a) Based on four direct 1976, 1977 studies listed immediately below. | |
| | | | (b) Value changed subsequent to publication to allow for effect of small C ₂ H ₆ impurity see Watson's review (1977) | |

Changed from NASA 1010: The values reported from the absolute rate coefficient studies for k at 298 K range from 0.99 to 1.48 x 10⁻¹³ with a mean value of 1.16 x 10⁻¹³. However, based upon the stated confidence limits reported in each study, the range of values far exceeds that to be expected. A preferred average value of 1.05 x 10⁻¹³ can be determined from the absolute rate coefficient studies for k at 298 K by giving equal weighting to the values reported in (Lin et al (1978a), Watson et al (1976), Manning and Kurylo (1977), Whytock et al (1977), Zahniser et al (1978), Michael and Lee (1977), and Keyser (1978)). The values derived for k at 298 K from the competitive chlorination studies (Lin et al (1978a), Knox and Nelson (1959), Knox (1955), and Pritchard et al (1955)) range from 0.95 - 1.13 x 10⁻¹³, with an average value of 1.02 x 10⁻¹³. The preferred value was obtained by taking a mean value from the most reliable absolute and relative rate coefficient studies.

There have been eight absolute studies of the activation energy. In general the agreement between most of these studies can be considered to be quite good. However, for a meaningful analysis of the reported values it is best to discuss them in terms of two distinct temperature regions, (a) below 300 K, and (b) above 300 K. Three resonance fluorescence studies have been performed between ~ 200 and 500 K (Whytock et al (1977), Zahniser et al (1978), and Keyser (1978)) and in each case a strong nonlinear Arrhenius behavior was observed. "his behavior tends to partially explain the large variance in the values of E/R reported between those other investigators who only studied this reaction below 300 K (Watson et al (1976), and Manning and Kurylo (1977)) and those who only studied it above 300 K (Clyne and Walker (1973), Poulet et al (1974), and Lin et al (1978a)). The agreement below 300 K is very good, with values of (a) E/P ranging from 1229-1320 K, and (b) k (230 K) ranging from (2.64 - 3.32) x 10⁻¹⁴. The mean of

the two discharge flow (Zahniser et al (1978) and Keyser (1978) results is 2.67×10^{-14} , while the mean of the three flash photolysis (Watson et al (1976), Manning and Kurylo (1977) and Whytock et al (1977) results is 3.19×10^{-14} . There have not been any absolute studies at stratospheric temperatures other than those which utilized the resonance fluorescence technique. Above 300 K the three resonance fluorescence studies reported (a) "averaged" values of F/R ranging from 1530 - 1623 K, and (b) values for k (500 K) ranging from $(7.74 - 8.76) \times 10^{-13}$. Three mass spectrometric studies have been performed above 300 K with E/R values ranging from 1409 - 1790 K. The data of Poulet et al (1974) are sparse and scattered, that of Clyne and Walker (1973) show too strong a temperature dependence (compared to all other absolute and competitive studies) and k (298) is $\sim 20\%$ higher than the preferred value at 298 K, while that of Lin et al is in fair agreement with the resonance fluorescence results. In conclusion, it should be stated that the best value of k from the absolute studies, both above and below 300 K, is obtained from the resonance fluorescence studies.

The competitive chlorination results differ from those obtained from the absolute studies in that linear Arrhenius behavior is observed. This difference is the major discrepancy between the two types of experiments. The values of E/R range from 1503 to 1530 K, and k (230 K) from $(2.11 - 2.54) \times 10^{-14}$ with a mean value of 2.27×10^{-14} . The preferred value is an expression which attempts to best fit the results obtained between 200 and 300 K from all sources. The average value of k at 298 K is 1.04×10^{-13} , and at 230 K is 2.70×10^{-14} . (These averages include results from the three competitive chlorination systems): $k = 9.94 \times 10^{-12} \exp(-1359/T)$. This expression essentially yields values similar to those obtained in the discharge flow-resonance fluorescence studies.

REFERENCES

- Clyne, W. A. A., and Walker, R. F., "Absolute Rate Constants for Elementary reactions in the Chlorination of CH_4 , CD_4 , CH_3Cl , CH_2Cl_2 , CHCl_3 , CCl_4 , and CBrCl_3 ," *J. Chem. Soc., Faraday Trans. 2*, **55**, 1547-1567 (1973)
- CODATA(1975). Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.
- Davis, D. D., Braun, W., and Bass, A. M., "Reactions of $\text{Cl}^2\text{P}_3/2$: Absolute Rate Constants for Reaction with H_2 , CH_4 , C_2H_6 , CH_2Cl_2 , C_2Cl_4 , and $\text{C-C}_6\text{H}_{12}$," *Int. J. Chem. Kinet.*, **2**, 101-114 (1970)
- Fettis, G. C., and Knox, J. E., "Rate Constants of Halogen Atom Reactions," G. Porter, Ed., *Progress in Reaction Kinetics* (Pergamon Press) **2**, 1-38 (1964)
- Keyser, L. F., "Absolute Rate and Temperature Dependence of the Reaction between Chlorine (^2P) Atoms and Methane," *J. Chem. Phys.*, **65**, 214-218 (1978)
- Knox, J. E., "Application of Gas Phase Partition Chromatography to Competitive Chlorination Reactions," *Chem. and Ind.* modified by Lin, Leu and DeVore (1978) 1631-1632 (1955)
- Knox, J. E., and Nalson, P. L., "Competitive Chlorination Reactions in the Gas Phase: Hydrogen and C_1 - C_5 Saturated Hydrocarbons," *Trans. Faraday Soc.*, **55**, 937-946 (1959)

- Lia, C. L., Liu, M. T., and DeMore, W. B., "Rate Constant for the Reaction of Atomic Chlorine with Methane," *J. Phys. Chem.* **82**, 1772-1777 (1978)
- Manning, R. G., and Kurylo, M. J., "Flash Photolysis Resonance Fluorescence Investigation of the Temperature Dependencies of the Reaction of $\text{Cl}(^2\text{P})$ Atoms with CH_4 , CH_3Cl , CH_3F , CH_3I , and C_2H_6 ," *J. Phys. Chem.* **81**, 291-296 (1977)
- Michael, J. V., and Lee, J. H., "Selected Rate Constants for H_2 , H_2O , and Cl Atoms with Substrates at Room Temperatures," *Chem. Phys. Lett.* **51**, 303-306 (1977)
- NASA WP-1010, "Chlorofluoromethanes and the Stratosphere" R. D. Hudson, Editor, August 1977 This reference contains the NASA (1977) rate constant recommendations-
- NASA (1979), Recommendations of the NASA Panel for Data Evaluation, published in NASA PP 1049 "The Stratosphere: Present and Future," R. D. Hudson and E. L. Reed, Editors, Dec. 1979 (report of the June 1979 Harpers Ferry Workshop)
- Poulet, G., Le Bras, G., and Combourieu, J., "Étude Cinétique des Réactions du Chlore Atomique et du Radical ClO Avec le Méthane Par la Technique du Réacteur à Écoulement Rapide, Couplé à un Spectromètre de Masse," *J. Chim. Phys.* **71**, 101-106 (1974)
- Pritchard, R. G., Pyke, J. B., and Trotman-Dickenson, A. F., "The Study of Chlorine Atom Reactions in the Gas Phase," *J. Am. Chem. Soc.* **77**, 2629-2633 (1955)
- Vatson, B. L., "Rate Constants for Reactions of ClO_x of Atmospheric Interest," *J. Phys. Chem. Ref. Data* **6**, 871-918 (1977)
- Vatson, B., Machado, G., Fischer, S., and Davis, D. D., "A Temperature Dependence Kinetics Study of the Reaction of $\text{Cl}(^2\text{P}_{3/2})$ with C_2H_4 , CH_4 , and H_2O_2 ," *J. Chem. Phys.* **65**, 2126-2138 (1976)
- Whytock, D. A., Lee, J. H., Michael, J. V., Payne, W. A., and Stief, L. J., "Absolute Rate of the Reaction of $\text{Cl}(^2\text{P})$ with Methane from 200-500 K," *J. Chem. Phys.* **66**, 2690-2695 (1977)
- Zahniser, M. S., Berquist, B. M., and Kaufman, F., "Kinetics of the Reaction $\text{Cl} + \text{CH}_4 \rightarrow \text{CH}_3 + \text{HCl}$ from 200 to 500 K," *Int. J. Chem. Kinet.* **10**, 15-25 (1978)
- R. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Reaction/Reference
Temp
Range/K
Reaction Rate Constant
k/cm³molecule⁻¹s⁻¹
Uncert Factor
at 298K, notes

| | | | | |
|-------|--|------------------------|---|------|
| 35,58 | Cl + C ₂ H ₆ → HCl + C ₂ H ₅ | ΔH (298) = - 22 kJ/mol | | |
| | CODATA (1979) eval | 220-350 | 7.7 x 10 ⁻¹¹ exp(-(90±100)/T) | 1-15 |
| | Manning, Kurylo (1977) | 222-322 | (7.29 ± 1.23) x 10 ⁻¹¹ exp(-60 ± 44/T) | |
| | Lewis, et al (1979) | 220-694 | 8.3 x 10 ⁻¹¹ exp(-130/T) | |

Recommended expression gives the best fit to the data between 220 and 350 K reported in these two studies

REFERENCES

- CODATA(1979). Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.
- Lewis, R. L., Sander, S., Wagner, S. J., and Watson, R. T., Manuscript in preparation, Jet propulsion Laboratory, Pasadena, CA (1979)
- Manning, F. G., and Kurylo, M. J., "Flash Photolysis Resonance Fluorescence Investigation of the Temperature Dependencies of the Reaction of Cl(2p) Atoms with CH₄, CH₃Cl, CH₃F, CH₃F₂, and C₂H₆," J. Phys. Chem. **81**, 291-296 (1977)

F. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Temp. Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncert. Factor at 298K, notes |
|-------|--|------------------|--|----------------------------------|
| 38.64 | Cl + CH ₃ Cl → CH ₂ Cl + HCl | | ΔB (298) = - 7 kJ/mol | |
| | NASA (1979) eval | 200-300 | 3.4 x 10 ⁻¹¹ exp(-(1256±200)/T) | 1.2 |
| | CODATA (1979) eval | 233-350 | 3.4 x 10 ⁻¹¹ exp(-(1260±200)/T) | 1.25 |
| | Clyne, Walker (1973) | 300-604 | 2.1 x 10 ⁻¹⁰ exp(-(1767±70)/T) | |
| | Watson, et al (1978) | 245-350 | 3.7 x 10 ⁻¹¹ exp(-(1287±150)/T) | |
| | Manning, Kurylo (1977) | 233-322 | 3.36 x 10 ⁻¹¹ exp(-(1250±57)/T) | |

New entry. The results reported by all three groups (Clyne and Walker (1973), Watson et al (1978) and Manning and Kurylo (1976)) are in good agreement at 298 K. However, the value of the activation energy measured by Watson et al and Manning et al is significantly lower than that measured by Clyne and Walker. Both groups of workers measured the rate constant for the Cl + CH₃Cl and similarly, the activation energy measured by Watson et al and Manning et al was significantly lower than that measured by Clyne and Walker. It is suggested that the discharge flow-mass spectrometric technique is subject to a systematic error, and it is recommended that the flash photolysis results be used for stratospheric calculations in the 200-300 K temperature range (see discussion of the Cl + CH₄ studies). In the discussion of the Cl + CH₄ reaction it was suggested that some of the apparent discrepancy between the results of Clyne and Walker and the flash photolysis studies can be explained by nonlinear Arrhenius behavior. However, it is less likely that this can be invoked for this reaction as the pre-exponential A-factor (as measured in the flash photolysis studies) is already ~3.5 x 10⁻¹¹ and the significant curvature which would be required in the Arrhenius plot to make the data compatible would result in an unreasonably high value for A (> 2 x 10⁻¹⁰).

REFERENCES

- Clyne, W. A. A., and Walker, R. F., "Absolute Rate Constants for Elementary Reactions in the Chlorination of CH₄, CD₄, CH₃Cl, CH₂Cl₂, CHCl₃, CCl₄, and CBrCl₃," J. Chem. Soc., Faraday Trans. I **69**, 1547-1567 (1973)
- CODATA(1979). Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.
- Manning, R. G., and Kurylo, M. J., "Flash Photolysis Resonance Fluorescence Investigation of the Temperature Dependencies of the Reaction of Cl(²P) Atoms with CH₄, CH₃Cl, CH₃F, CH₃F₂, and C₂H₆," J. Phys. Chem. **81**, 291-296 (1977)

NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," E. B. Hudson and E. L. Reed, Editors, Dec. 1975 (report of the June 1975 Harpers Ferry Workshop).

Watson, E. L., Mochade, E. S., Schliff, E. L., and Davis, D. D., 1979. Manuscript in preparation, Jet Propulsion Laboratory, Pasadena, California.

E. F. Sampson
June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Temp. Range/K | Reaction Rate Constant $k/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$ | Uncert. Factor at 298K, notes |
|--------|----------------------------------|------------------|--|----------------------------------|
| | | | | |
| 387,56 | $F + CH_4 \rightarrow HF + CH_3$ | | $\Delta H (298) = -139 \text{ kJ/mol}$ | |
| | NASA (1979) eval | 280-300 | $3.0 \times 10^{-10} \exp(-4000/300/T)$ | 2 |
| | CODATA (1979) eval | 280-450 | $3.0 \times 10^{-10} \exp(-4000/300/T)$ | 1.5 |
| | Wagner, et al (1971) | 298-450 | $5.5 \times 10^{-10} \exp(-579/T)$ | |
| | Clyne, et al (1973) | 300 | 6×10^{-11} | |
| | Kospe, Wagner | 298 | 7.2×10^{-11} | |

New entry. The three absolute rate coefficients determined by Wagner et al (1971), Clyne et al (1973) and Kospe and Wagner (1972) at 298 K are in good agreement; however, this may be somewhat fortuitous as the ratios of $k(F + H_2)/k(F + CH_4)$ determined by these same groups can only be considered to be in fair agreement, 0.23, 0.42 and 0.98. The values determined for $k (298)$ from the relative rate coefficient studies are also in good agreement with those determined in the absolute rate coefficient studies, and the value of 0.42 reported for $k(F + H_2)/k(F + CH_4)$ by Feen and Reid (1971) is in good agreement with that reported by Clyne et al. The preferred value of 8.0×10^{-11} for $k (298)$ is a weighted mean of all the results. The magnitude of the temperature dependence is somewhat uncertain. The preferred Arrhenius parameters are based on the data reported by Wagner et al, and Feen and Reid, and the preferred Arrhenius parameters of the $F + H_2$ reaction. This reaction has recently been reviewed by both Feen and Kaufman (1975) and Jones and Skolnik (1976). A-factor may be too high

REFERENCES

- Clyne, M. A. A., McKenney, D. J., and Walker, R. P.,
 "Reaction Kinetics of Ground State Fluorine, $F(^2P)$, Atoms,
 I. Measurement of Fluorine Atom Concentrations and the
 Rates of Reactions $F + CHF_3$ and $F + Cl_2$ using Mass
 Spectrometry," Can. J. Chem. **51**, 3596-3604 (1973)
- CODATA(1979). Recommendations of the CODATA Task Group on Chemical
 Kinetics. To be published in the Journal of Physical and Chemical
 Reference Data.
- Feen, R., and Kaufman, M., "Kinetics of Gaseous Fluorine
 Reactions," Progress in Reaction Kinetics, **8**, 81 (1975)

Foon, R., and Reid, G. P., "Kinetics of the Gas Phase Fluorination of Hydrogen and Alkanes," Trans. Faraday Soc. **67**, 3913-3920 (1971)

Jones, W. E., and Shelnik, E. G., "Reactions of Fluorine Atoms," Chem. Rev. **76**, 563-592 (1976)

Kespe, K. L., and Wanner, J., "Study of Some Fluorine Atom Reactions using a Chemical Laser Method," Chem. Phys. Lett. **12**, 560-563 (1972)

NASA (1979), Recommendations of the NASA Panel for Data Evaluation, published in NASA BP 1049 "The Stratosphere: Present and Future," E. D. Hudson and E. I. Reed, Editors, Dec. 1975 (report of the June 1975 Harpers Ferry Workshop).

Wagner, E. G., Wernetz, J., and Zetzsch, G., "On the Reaction of F Atoms with Methane," Anal. Assoc. Quim. Argentina, **23**, 165-177 (1971)

D. P. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Reaction/Reference
Temp
Range/K
Reaction Rate Constant
k/cm³molecule⁻¹s⁻¹
Uncert Factor
at 298K, notes

36.36 ClO + ClO → Cl + ClO₂ (a)
- Cl₂ + O₂ (b)
- nClO + Cl (c)
NASA (1979) eval

ΔH (298) = 6 kJ/mol
- 204 kJ/mol
- 14 kJ/mol
no recommendation; see note

No recommendation at present; however, if values are needed for modelling purposes, use those shown in NASA 1010, i.e., k(ClO + ClO → Cl + ClO₂) = 1 x 10⁻¹² exp(-1238/T); k(ClO + ClO → Cl₂ + O₂) = 5 x 10⁻¹³ exp(-1238/T). The data base used for this evaluation has been discussed in detail by Watson (1977). At present no recommendation is given for the ClO + ClO reaction as the partitioning between the channels (especially the temperature dependence of the partitioning) is not well established. Cox and Derwent (1979) have recently written a paper concerning the absolute values of the following channels: ClO + ClO → Cl + ClO₂; ClO + ClO → Cl₂ + O₂; ClO + ClO → Cl + ClO₂; ClO + ClO → Cl + ClO₂. This data needs to be thoroughly evaluated before recommending any new values for these reaction pathways

REFERENCES

Cox, P. A., and Derwent, P. G., "Kinetics of Chlorine Oxide Radical Reactions using Modulated Photolysis, Part 10 - Disproportionation of ClO in the Cl₂ Photosensitized Decomposition of Ozone," J. Chem. Soc. Faraday Trans. I 75, 1635-1647 (1979)

NASA RP-1010: "Chlorofluoromethanes and the Stratosphere"

P. D. Hudson, Editor, August 1977 This reference contains the NASA (1977) rate constant recommendations.

NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," P. D. Hudson and E. L. Reed, Editors, Dec. 1979 (report of the June 1979 Harpers Ferry Workshop).

Watson, R. T., "Rate Constants for Reactions of ClO_x of Atmospheric Interest," J. Phys. Chem. Ref. Data 6, 871-918 (1977)

R. P. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Reaction/Reference
 Temp
 Range/K
 Reaction Rate Constant
 $\text{k/cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
 Uncert Factor
 at 298K, notes

| | | | | |
|---------|--|--|--|------------|
| 36,36Br | $\text{Cl} \cdot + \text{Br}_2 \rightarrow \text{Br} \cdot + \text{Cl}_2$ (a) $\rightarrow \text{Br} \cdot + \text{Cl} \cdot + \text{Cl}_2$ (b) | ΔH (298) = - 14 kJ/mol = 5 kJ/mol | | |
| | NASA (1979) eval | 200-300 | $k_a = 6.7 \times 10^{-12} \exp((0 \pm 250)/T)$ $k_b = 6.7 \times 10^{-12} \exp((0 \pm 250)/T)$ | 1 5 1-5 |
| | CODATA (1979) eval | 298 | $k_a = 6.7 \times 10^{-12}$ $k_b = 6.7 \times 10^{-12}$ | 2 2 |
| | Clyne, Watson (1977) | 298 | $k_a = 6.7 \pm 1.7 \times 10^{-12}$ $k_b = (6.7 \pm 1.7) \times 10^{-12}$ | |
| | Basco, Dogra (1971) | 300 | 2.5×10^{-12} Products assumed to be $\text{BrCl} + \text{Cl}_2$ | |

Unchanged from NASA 1010. The results reported by Clyne and Watson (1977) and Basco and Dogra (1971) differ not only in the magnitude of the rate constants, but also in the interpretation of the reaction mechanism. The preferred value is that reported by Clyne and Watson. The temperature dependence for such processes is expected to be small, as for $\text{Br} \cdot + \text{Br}_2$. Although the second reaction channel is shown proceeding directly to $\text{Br} \cdot + \text{Cl} \cdot + \text{Cl}_2$, it may proceed through $\text{Br} \cdot + \text{Cl} \cdot + \text{Cl}_2 \rightarrow \text{Br} \cdot + \text{BrCl} + \text{Cl}_2$ or $\text{Cl} \cdot + \text{BrCl} + \text{Cl}_2$ (ΔH° unknown).

REFERENCES

Basco, M., and Dogra, S. K., "Reactions of Halogen Oxides Studied by Flash Photolysis III. The Production and Reactions of $\text{Br} \cdot$ and $\text{Cl} \cdot$ Radicals in the Halogen-Sensitized Decomposition of Chlorine Dioxide," *Proc. Roy. Soc. Lond. A*, **323**, 417-429 (1971)

Clyne, M. A., and Watson, R. T., "Kinetic Studies of Diatomic Free Radicals using Mass Spectrometry. Part 4. The $\text{Br} \cdot + \text{Cl}_2$ and $\text{Br} \cdot + \text{Cl} \cdot$ Reactions," *J. Chem. Soc., Faraday Trans. I*, **73**, 1169-1187 (1977)

CODATA (1979): Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the *Journal of Physical and Chemical Reference Data*.

NASA RP-1010, "Chlorofluoromethanes and the Stratosphere" P. D. Hudson, Editor, August 1977 This reference contains the NASA (1977) rate constant recommendations.

NASA (1979). Recommendations of the NASA Panel for Data Evaluation,
published in NASA RP 1049 "The Stratosphere: Present and Future,"
W. D. Hudson and E. L. Read, Editors, Dec. 1979 (report of the
June 1979 Warners Ferry Workshop).
P. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Temp. Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncert. Factor at 298K, notes |
|---------|-------------------------------|------------------|--|----------------------------------|
| 36F.36F | F6 + F6 → 2F + O ₂ | | ΔH (298) = - 59 kJ/mol | |
| | NASA (1979) eval | 200-300 | 1.5 x 10 ⁻¹¹ | 3 |
| | CODATA (1979) eval | 298 | 1.5 x 10 ⁻¹¹ | 2 |
| | Clyne, Watson (1974) | 258 | (6.5±2.8) x 10 ⁻¹² | |
| | Wagner, et al (1972) | 258 | 3.3 x 10 ⁻¹¹ | |

New entry. Although the value of k(F6 + F6) reported by Clyne and Watson (1974) was obtained in a more direct manner than that of Wagner et al (1972), and as such is less susceptible to error due to the presence of complicating secondary reactions and thus would normally be preferred, the value to be recommended in this assessment is a weighted average of the two studies. From the data of Wagner et al it can be seen that the dominant reaction channel is that producing 2F + O₂. However, their data base is not adequate to conclude that it is the only process

REFERENCES

- Clyne, M. A. A., and Watson, R. T., "Kinetic Studies of Diatomic Free Radicals using Mass Spectrometry Part I. System Description and Applications to F Atoms and F₂ Radicals," J. Chem. Soc., Faraday Trans. I **70**, 1109-1123 (1974)
- CODATA(1979). Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.
- NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA SP 1049 "The Stratosphere: Present and Future," E. D. Hudson and E. L. Reed, Editors, Dec. 1979 (report of the June 1975 Harpers Ferry Workshop).
- Wagner, M. G., Zetzsch, C., and Varnatz, J., "Gas-Phase Preparation of CF Radicals by Reaction of Fluorine Atoms with Ozon," Ber. Bunsenges. Phys. Chem. **76**, 526-530 (1972)
- E. F. Harrison
June 1979

Uncert Factor
at 298K, notes

| P_0 | Reaction/Reference | Temp. Range/K | Reaction Rate Constant $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | Uncert. Factor at 298K, notes |
|-------|---|---------------|--|----------------------------------|
| 55.45 | $\text{Cl}_2 + \text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_2 + \text{Cl}_2$ | | $\Delta H (298) = -264 \text{ kJ/mol}$ | |
| | NASA (1979) eval | 200-300 | $1 \times 10^{-12} \exp(-3700/T)$ | |
| | | 298 | 4×10^{-18} | |

Unchanged from NASA 1010. These upper limits are based on the data of Walker (reported by Clyne and Watson (1974e)). The upper limits shown for k (298) were estimated from data collected at either 587 K or 670 K. The Arrhenius expressions were estimated based on this ~ 600 K data by choosing the "A factor"

REFERENCES

- Clyne, W. A. Ac., and Watson, R. To, "Kinetic Studies of Diatomic Free Radicals using Mass Spectrometry Part 2, Rapid Bimolecular Reactions Involving the ClM X2O Radical," J. Chem. Soc., Faraday Trans. I 70, 2250-2259 (1974a)
- NASA RP-1010, "Chlorofluoromethanes and the Stratosphere" R. D. Hudson, Editor, August 1977 This reference contains the NASA (1977) rate constant recommendations.
- NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," R. D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the June 1979 Harpers Perry Workshop).
- R. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS
Reaction/Reference

Uncert Factor
at 298K, notes

| No | Temp Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncert Factor at 298K, notes |
|--------|-----------------|--|---------------------------------|
| 36, 56 | 200-300 298 | $\pm 1 \times 10^{-12} \exp(-3700/T)$ $\pm 4 \times 10^{-18}$ | |

Cl + CH₄ - products
NASA (1979) eval

Unchanged from NASA 1010. These upper limits are based on the data of Walker (reported by Clyne and Watson (1974a)). The upper limits shown for k (298) were estimated from data collected at either 587 K or 670 K. The Arrhenius expressions were estimated based on this ~ 600 K data by choosing the "A factor."

REFERENCES

- Clyne, M. A., and Watson, R. T., "Kinetic Studies of Diatomic Free Radicals using Mass Spectrometry Part 2. Rapid Bimolecular Reactions Involving the Cl + X² Radical," J. Chem. Soc., Faraday Trans. I 70, 2250-2259 (1974a)
- NASA RP-1010, "Chlorofluoromethanes and the Stratosphere" R. D. Hudson, Editor, August 1977 This reference contains the NASA (1977) rate constant recommendations.
- NASA (1979)- Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," R. D. Hudson and E. L. Reed, Editors, Dec. 1979 (report of the June 1975 Harpers Ferry Workshop).

R. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Uncert Factor
at 298K, notes

Reaction/Reference
Temp-
Range/K
Reaction Rate Constant
 $k/cm^3 molecule^{-1} s^{-1}$

No

36,57 $Cl_2 + C_2H_4 \rightarrow$ products
Clyne, Watson (1974a)

670 $k \leq 1 \times 10^{-15}$

Note that this is an upper limit - no reaction was observed

REFERENCES

Clyne, W. A. A., and Watson, R. T., "Kinetic Studies of
Diatomic Free Radicals using Mass Spectrometry, Part 2,
Rapid Bimolecular Reactions Involving the Cl_2 Radical,"
J. Chem. Soc., Faraday Trans. 1 70, 2250-2259 (1974a)

R. F. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No | Reaction/Reference | Temp | Reaction Rate Constant | Uncert Factor at 298K, notes |
|--------|--|---------|--|---------------------------------|
| | | Range/K | k/cm ³ molecule ⁻¹ s ⁻¹ | |
| 36,56a | Cl + C ₂ H ₂ → products Clyne, Watson (1974a) | 670 | k ≤ 1 × 10 ⁻¹⁵ | |

Note that this is an upper limit - no reaction was observed

REFERENCES

Clyne, M. A. and Watson, R. T., "Kinetic Studies of
Diatomic Free Radicals using Mass Spectrometry Part 2,
Rapid Bimolecular Reactions Involving the ClO X²Π Radical,"
J. Chem. Soc., Faraday Trans. 1 **70**, 2250-2259 (1974a)

R. F. Hampson
May 1976

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Uncert Factor
at 298K, notes

Reaction Rate Constant
 $k/cm^3 \text{ molecule}^{-1} s^{-1}$

Temp
Range/K

Reaction/Reference

| No | Reaction/Reference | Temp Range/K | Reaction Rate Constant $k/cm^3 \text{ molecule}^{-1} s^{-1}$ | Uncert Factor at 298K, notes |
|--------------|---|-----------------|---|---|
| | | | | |
| 303Br, 303Br | $Br\dot{O} + Br\dot{O} \rightarrow 2Br + O_2$ (a) $\rightarrow Br_2 + O_2$ (b) | | | |
| | NASA (1979) eval | 290-300 | $\Delta H(298) = -26 \text{ kJ/mol}$ $= -256 \text{ kJ/mol}$ $k_a = 1.0 \times 10^{-12} \exp((244 \pm 150)/T)$ $k_b = 1.8 \times 10^{-13} \exp((244 \pm 150)/T)$ $k = 2.8 \times 10^{-12} \exp((0 \pm 500)/T)$ $k = 1.13 \times 10^{-12} \exp((244 \pm 100)/T)$ $k = 3.2 \times 10^{-12}$ $k = 1.1 \times 10^{-12}$ $k = 2.6 \times 10^{-11} \exp(-450/T)$ $k = 0.65 \times 10^{-12}$ (a) $-d[Br\dot{O}]/dt = 2 k[Br\dot{O}]^2$ | 1.25 (a) 1.25 (a) 1.25 (a) (a) (a) (a) (a) (a) |
| | CODATA (1979) eval | 220-440 | | |
| | Sander, Watson (1979) | 223-398 | | |
| | Clyne, Watson (1975) | 298 | | |
| | Basco, Dogra (1971) | 298 | | |
| | Clyne, Cruse (1970) | 293 | | |
| | Clyne, Coxon (1968) | 298 | | |

Changed from NASA 1010 due to new data. Four of the five studies (Clyne and Coxon (1968), Clyne and Cruse (1970), Basco and Dogra (1971), and Sander and Watson (1978)), monitored the $Br\dot{O}$ radical concentration using ultraviolet absorption spectrometry. As the reaction being studied was second order in $[Br\dot{O}]$ knowledge of σ was required in order to determine k . There is substantial disagreement between the values of σ . Although the magnitude of σ is dependent upon the particular transition and instrumental parameters such as spectral bandwidth, the most probable reason for the differences is that the technique (based on reaction stoichiometries) used to determine σ in the early studies (Clyne and Coxon, Clyne and Cruse, and Basco and Dogra) was used incorrectly (discussed by Clyne and Watson (1975)). The most recent study (Sander and Watson (1978)) used the same technique to determine σ , but avoided the problems. In three of the studies (Clyne and Coxon, Basco and Dogra, and Sander and Watson) there is good agreement in the reported values of k/σ ; however, this may be somewhat fortuitous as σ is expected to vary somewhat from study to study. The preferred value for k at 298 K is taken to be an average of the values reported by Clyne and Watson (the mass spectrometric study where knowledge of σ is not required) and Sander and Watson (the recent absorption study). There was no observable pressure dependence (50-600 torr) in the recent flash photolysis study. From the values of k reported by Clyne and Watson and Sander and Watson, it can be stated that the $Br\dot{O} + Br\dot{O}$ reaction exhibits no pressure dependence within the range 1-600 torr. The recent flash photolysis study determined the temperature dependence of both k/σ and σ independently. The preferred Arrhenius expression uses the temperature dependence reported by Sander and Watson, and the pre-exponential A-factor was adjusted to yield the preferred value at 298 K. Although the partitioning of the total rate constant into its two components, k_1 and k_2 , was quantitatively studied at 298 K by Sander and Watson, and the ratio $k_1/(k_1 + k_2)$ reported to be 0.85 \pm 0.5, it is not clear whether this ratio would be expected to exhibit a temperature dependence (the values shown in the table assume the partitioning is invariant with temperature). Whereas the ratio of k_1/k_2 reported by Sander and Watson is in good agreement with that estimated by Cruse (1971), the temperature dependence of $k_1 + k_2$ disagrees.

REFERENCES

- Basco, M., and Bogra, S. K., "Reactions of Halogen Oxides Studied by Flash Photolysis III. The Production and Reactions of BrO and ClO Radicals in the Halogen-Sensitized Decomposition of Chlorine Dioxide," *Proc. Roy. Soc. Lond. A*, **323**, 417-429 (1971)
- Clyne, M. A. A., and Coxon, J. A., "Kinetics Studies of Oxyhalogen Radical Systems," *Proc. Roy. Soc., (London)* **A 303**, 207-231 (1968)
- Clyne, M. A. A., and Cruse, E. W., "Rates of Elementary Reaction Involving the BrO(X²Π) and IO(X²Π) Radicals. Part I.-Formation and Decay of the BrO Radical," *Trans. Faraday Soc.*, **66**, 2214-2226 (1970)
- Clyne, M. A. A., and Watson, R. T., "Kinetics Studies for Diatomic Free Radicals using Mass Spectrometry Part 3 - Elementary Reactions Involving BrO(X²Π) Radicals," *J. Chem. Soc., Faraday Trans. 1*, **71**, 336-350 (1975)
- CCDATA(1979). Recommendations of the CCDATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.
- Cruse, E. W., Ph.D. Thesis, Queen Mary College, London University, (1971)
- NASA RP-1010, "Chlorofluoromethanes and the Stratosphere" R. D. Hudson, Editor, August 1977 This reference contains the NASA (1977) rate constant recommendations.
- NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," R. D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the June 1979 Harpers Ferry Workshop)
- Sander, S. P., and Watson, R. T., 1978, Manuscript in preparation.
- R. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No | Reaction/Reference | Temp Range/K | Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹ | Uncert Factor at 298K, notes |
|-------|--|-----------------|---|---|
| 50.4 | CH ₃ ^o + O ₂ → CH ₂ ^o + HO ₂ (1) | | ΔH (298) = -121 kJ/mol | |
| 50.9 | CH ₃ ^o + NO → CH ₃ NO (2a) | | -170 kJ/mol | |
| | → CH ₂ ^o + NO (2b) | | -114 kJ/mol | |
| 50.10 | CH ₃ ^o + NO ₂ → CH ₃ NO ₂ (3a) | | -167 kJ/mol | |
| 50.45 | CH ₃ ^o + CO → products (4) | | -236 kJ/mol | |
| | NASA (1979) eval | 200-300 | k ₁ = 5 x 10 ⁻¹³ exp(-(2000+750)/T) | 2 |
| | CODATA (1979) eval | 300-450 | k ₁ = 5 x 10 ⁻¹³ exp(-(2000+1000)/T) | 4 |
| | Barker, et al (1977) | 396-442 | k ₁ = 5 x 10 ⁻¹³ exp(-2000/T) | |
| | Bett, Robinson (1979) | 363-433 | k ₁ = 1.7 x 10 ⁻¹² exp(-2400/T) | |
| | Reicklen (1973) | 298 | k ₁ ~ 3 x 10 ⁻¹⁸ ~ 1.6 x 10 ⁻¹³ exp(-3300/T) | |
| | | 298 | k ₂ ~ 8 x 10 ⁻¹⁴ k ₁ /k ₂ = 4.7 x 10 ⁻⁵ ±20% | ratio probably is smaller at 220K |
| | | 298 | k _{2b} /k ₂ = 0.145 ±0.015 | |
| | | 363 | k ₂ /k ₃ = 1.2 ±0.1 | |
| | | 403 | k _{2a} /k _{3a} = 1.1 = 2.7 | |
| | | 298 | k _{3a} /k ₃ = 0.9 ±0.1 | k _{3a} /k _{3b} probably constant 300-400K |
| | | 298 | k _{3b} /k ₃ = 0.1 ±0.01 | |
| | Demerjian, et al (1974) review | 298-423 | k ₄ /k ₂ = 5 x 10 ⁻⁴ k ₁ = 1.6 x 10 ⁻¹⁷ ~ 4.2 x 10 ⁻¹³ exp(-3000/T) | |
| | | 300 | adjusted to fit C ₄ H ₁₀ /NO _x simulation studies | |
| | | | k _{2a} = 1.7 x 10 ⁻¹³ k _{2b} /k _{2a} = 0.17 k _{3a} = 3.3 x 10 ⁻¹³ k _{3b} /k _{3a} = 0.1 k _{2a} ~ 3 x 10 ⁻¹¹ k _{2b} ~ 7 x 10 ⁻¹² | |
| | Bett, McCulloch, Milne (1975) | 393-473 | | |

The recommended A-factor and E/R values for k₁ are those determined by Barker et al (1977), who measured the ratio k(CH₃ + O₂)/k(CH₃ + NO₂ + M) from 396 to 424K. Recent results on this same system have been reported by Batt and Robinson (1979). Although these new results yield a higher A-factor and somewhat higher E/P, they are consistent with the results of Barker et al over the limited temperature range studied. The k(298) value is calculated from the recommended A-factor and E/R. Further work over a wider temperature range is needed.

REFERENCES

- Barker, J. R., Benson, S. W., and Golden, D. M., "The Decomposition of Dimethyl Peroxide and the Rate Constant for $\text{CH}_3\text{O} + \text{O}_2 \rightarrow \text{CH}_3\text{O} + \text{HO}_2$," *Int. J. Chem. Kinet.* **2**, 31-53 (1977)
- Batt, L., and Robinson, G. W., "Reaction of Methoxy Radicals with Oxygen: Using Dimethyl Peroxide as a Thermal Source of Methoxy Radicals," *Int. J. Chem. Kinet.* **11**, 1045-1053 (1979)
- Batt, L., McCulloch, R. D., and Milne, R. T., "Thermochemical and Kinetic Studies of Alkyl Nitrites (RNO) - D(RD-NO), The Reactions between RNO and NO , and the Decomposition of RNO ," *Int. J. Chem. Kinet.*, Symp. No. 1, 441-461 (1975)
- CDATA (1979). Recommendations of the CDATA Task Group on Chemical Kinetics To be published in the Journal of Physical and Chemical Reference Data.
- Demerjian, K. L., Kerr, J. A., and Calvert, J. G., "The Mechanism of Photochemical Smog Formation," *Adv. Environ. Sci. Technol.* **4**, 1-262 (1974)
- J. N. Pitts, Jr., and P. L. Metcalfe, editors, Wiley-Interscience
- Heicklen, J., "Photochemical and Rate Data for Methyl Nitrite, Methoxy and Methylperoxy," *Chemical Kinetics Data Survey V. Sixty-six Contributed Rate and Photochemical Data Evaluations on Ninety-four Reactions*, NBSIR 73-206, D. Garvin, Ed., National Bureau of Standards, Washington, D.C. (1973) pages 43-48
- NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," V. D. Hudson and E. L. Peed, Editors, Dec. 1979 (report of the June 1979 Harpers Ferry Workshop).
- P. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Uncert Factor
at 298K, notes

| No | Reaction/Reference | Temp. Range/K | Reaction Rate Constant $k/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$ | Uncert Factor at 298K, notes |
|-------|---|------------------|---|---------------------------------|
| 51.51 | $2\text{CF}_3\text{O}_2 \rightarrow 2\text{CF}_3\text{O} + \text{O}_2$ (a) $\rightarrow \text{CF}_3\text{OH} + \text{CH}_2\text{O} + \text{O}_2$ (b) $\rightarrow \text{CF}_3\text{OCH}_3 + \text{O}_2$ (c) | | $\Delta H(298) = 15 \text{ kJ/mol}$ $= -324 \text{ kJ/mol}$ $= -179 \text{ kJ/mol}$ | |
| | CODATA (1979) eval | 298 | $k = 4.6 \times 10^{-13} (k_a + k_b + k_c)$ $k_a/k = 0.33$ | 1-25 |
| | Parkes (1977) | 300 | $k_a = 1.6 \pm 0.4 \times 10^{-13}$ $k_b + k_c = 3.0 \pm 0.8 \times 10^{-13}$ | |
| | Anastasi, et al (1978) | 298 | $k = (4.4 \pm 1) \times 10^{-13}$ | |
| | Hochanadel, et al (1977) | 298 | $k = (3.8 \pm 0.7) \times 10^{-13}$ | |
| | Weaver, et al (1975) | 300 | $k_a/k = 0.43$ $k_b/k = 0.50$ $k_c/k = 0.07$ | |

The recommended value for the overall rate constant is taken from the work of Parkes (1977)

REFERENCES

- Anastasi, C., Smith, I., W., W., and Parkes, D. Ac. "Flash
 Photolysis Study of the Spectra of CH_3O_2 and $\text{C}(\text{CH}_3)_3\text{O}_2$
 Radicals and the Kinetics of their Mutual Reactions
 and with NO ," J. Chem. Soc., Faraday Trans. 1 **74**, 1693-1701
 (1978)
- CODATA(1979), Recommendations of the CODATA Task Group on Chemical
 Kinetics. To be published in the Journal of Physical and Chemical
 Reference Data.
- Hochanadel, C. J., Ghorale, J., Ac., Boyle, J., W., and Green, P. J.,
 "Absorption Spectrum and Rates of Formation and Decay of the CH_3O_2
 Radical," J. Phys. Chem. **81**, 3-7 (1977)
- Parkes, D. Ac., "Oxidation of Methyl Radicals at Room Temperature," Into J.
 Chem. Kinet. **9**, 451-469 (1977)

Beaver, J., Mesgher, J., Shortridge, R., and Heicklen, J., "The Oxidation of
p. Acetyl radicals," J. Photochem. 4, 341-360 (1975)
v. P. Hampson
June 1970

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Photochemical Data |
|-----|--------------------|--------------------|
|-----|--------------------|--------------------|

4. hv $O_2 + hv \rightarrow O(^3P) + O(^3P) \quad (1)$
 $\rightarrow O(^3P) + O(^1D) \quad (2)$

$\Delta H = 494 \text{ kJ/mol}; \lambda_{\text{threshold}} = 242 \text{ nm}$
 $\Delta H = 683 \text{ kJ/mol}; \lambda_{\text{threshold}} = 175 \text{ nm}$

NASA (1979) eval

The absorption spectrum of O_2 in the Schumann-Runge bands (175-200nm) has been re-examined recently by Frederick and Hudson (1979), who found some of the line widths to be smaller than those reported earlier by Ackerman and Blaume (1970). The recommended values are the new results of Frederick and Hudson, which will affect the calculations of solar flux penetration into the Earth's atmosphere in the 180-200 nm region. Due to the highly structured nature of the spectrum in question and due to the complications in the solar flux calculations, these results are not presented here; the reader is referred to the original publication of Frederick and Hudson. Uncertainty factor for photochemical rates is 1.4 for S-R bands and 1.05 for continua.

CODATA (1979) eval

$\beta_1 = 1 \quad 175 < \lambda < 200 \text{ nm}$
 $\beta_2 = 1 \quad 140 < \lambda < 175 \text{ nm}$

| Absorption cross sections | | |
|---|---|---------------------|
| $10^{-22} \text{ cm}^2 \text{ molecule}^{-1}$ | $10^{-22} \text{ cm}^2 \text{ molecule}^{-1}$ | 10^{24} g |
| 680-690 | 141 | 11.4 |
| 660-670 | 115 | 8.9 |
| 640-650 | 82.4 | 6.3 |
| 620-630 | 49.7 | 3.8 |
| 600-610 | 20.8 | 0.7 |
| 580-590 | 7.2 | |
| 570-575 | 2.7 | |

These values are taken from Ackerman (1971).

REFERENCES

Ackerman, M., "Ultraviolet Solar Radiation Related to Mesospheric Processes," 149-159 in "Mesospheric Models and Related Experiments" G. Fiocco, ed., Reidel Publ. Co., Dordrecht, Holland (1971)

Ackerman, M., and Blaine, P., "Structure of the Schumann-Runge Bands from the 0-0 to the 13-0 Band," J. Mol. Spectrosc. **25**, 72-82 (1970)

CODATA(1979). Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.

Frederick, J. E., and Hudson, R. D., "Predissociation Linewidths and Oscillator Strengths for the (2-0) to (13-0) Schumann-Runge Bands of O_2 ," J. Mol. Spectrosc. **74**, 247-258 (1979)

NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," R. D. Hudson and R. I. Reed, Editors, Dec. 1979 (report of the June 1975 Harpers Ferry Workshop).

R. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

No. Reaction/Reference

Photochemical Data

7. hv $\sigma_3 + h\nu \rightarrow \sigma(^1D) + \sigma_2(^1A)$

NASA (1979)eval

AE = 365 kJ/mol; $\lambda_{\text{threshold}} = 310 \text{ nm}$

The recommended values for the $\phi(^1D)$ quantum yield ϕ as a function of wavelength and temperature are given by the mathematical expression developed by Moortgat and Kudzus (1978). The expression fits their own data (Moortgat and Warneck, 1975; Moortgat et al, 1977; Arnold et al, 1977), as well as the low temperature data of Lin and DeMore (1973). The results agree within 10% with the data recommended in NASA EP-1010, which is only for 235 K. The mathematical expression is the following:

$$\phi(\lambda, T) = A(\tau) \arctan[B(\tau)(\lambda - \lambda_0(\tau))] + C(\tau)$$

Where: $\tau = T - 230$ is a temperature function with T given in Kelvin, λ is expressed in nm, and arctan in radians.

The coefficients $A(\tau)$, $B(\tau)$, $\lambda_0(\tau)$ and $C(\tau)$ are expressed as interpolation polynomials of the third order:

$$A(\tau) = 0.369 + 2.85 \times 10^{-4}\tau + 1.28 \times 10^{-5}\tau^2 + 2.57 \times 10^{-6}\tau^3$$

$$B(\tau) = -0.575 + 5.59 \times 10^{-3}\tau - 1.439 \times 10^{-5}\tau^2 - 3.27 \times 10^{-6}\tau^3$$

$$\lambda_0(\tau) = 308.20 + 4.4871 \times 10^{-2}\tau + 6.9360 \times 10^{-5}\tau^2 - 2.5452 \times 10^{-6}\tau^3$$

$$C(\tau) = 0.518 + 9.87 \times 10^{-4}\tau - 3.54 \times 10^{-5}\tau^2 + 3.91 \times 10^{-7}\tau^3$$

In the limits where $\phi(\lambda, T) = 1$, the quantum yield is set $\phi = 1$, and similarly for $\phi(\lambda, T) = 0$, the quantum yield is set $\phi = 0$.

The results of recent laser studies by Brock and Watson (private communication, 1979) are in good agreement with this recommendation. The recommended value for the quantum yield for $\phi(^1D)$ production at wavelength shorter than 300 nm is unity, as reported by Amimoto et al (1978) and Kajimoto and Cveticanovic (1979). The results of Fairchild et al (1978) as well as those of Sparks et al (1979) indicate, however, that the quantum yield at those wavelengths is about 0.9. This question requires further study. Uncertainty factor for photochemical rate is 1.4.

CODATA (1979) eval

Absorption cross sections

| $10^{-22} \text{ m}^2 \text{ cm}^{-1}$ | 10^{19} g | $10^{-22} \text{ m}^2 \text{ cm}^{-1}$ | 10^{19} g |
|--|---------------------|--|---------------------|
| 500-505 | 3.30 | 370-375 | 82.3 |
| 475-480 | 4.84 | 360-365 | 53.1 |
| 450-455 | 19.7 | 350-355 | 28.4 |
| 425-430 | 57.9 | 340-345 | 11.4 |
| 400-405 | 107 | 330-335 | 3.7 |
| 350-395 | 112 | 320-325 | 1.0 |
| 380-385 | 103 | | |

These values averaged over 500 cm^{-1} are taken from Ackerman (1971).

REFERENCES

- Ackerman, M., "Ultraviolet Solar Radiation Related to Mesospheric Processes," 149-159 in "Mesospheric Models and Related Experiments" G. Fiocco, ed., Reidel Publ. Co., Dordrecht, Holland (1971)
- Amisato, S., To. Force, A. P., and Wiesenfeld, J., "Ozone Photochemistry: Production and Deactivation of $\text{O}(^1\text{D}_2)$ Following Photolysis at 248 nm," *Chem. Phys. Lett.* **50**, 40-43 (1978)
- Arnold, L., Cones, P. J., and Moortgat, G. E., "Laser Flash Photolysis: Quantum Yield of $\text{O}(^1\text{D})$ Formation from Ozone," *Chem. Phys.* **24**, 211-217 (1977)
- CODATA(1975), Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.
- Fairchild, C. E., Stone, R. J., and Lawrence, G. M., "Photofragment Spectroscopy of Ozone in the UV Region 270-310 nm and at 600 nm," *J. Chem. Phys.* **52**, 3622-3638 (1978)
- Kadimoto, G., and Cvitanović, B. J., "Absolute Quantum Yield of $\text{O}(^1\text{D})$ in the Photolysis of Ozone in the Hartley Band," *Int. J. Chem. Kinet.* **11**, 605-612 (1979)
- Lin, C. L., and DeMore, W. E., " $\text{O}(^1\text{D})$ Production in Ozone Photolysis Near 3100 Å," *J. Photochem.* **2**, 161-164 (1973)
- Moortgat, G. E., and Kudzus, E., "Mathematical Expression for the $\text{O}(^1\text{D})$ Quantum Yields from the G_2 Photolysis as a Function of Temperature (230-320 K) and Wavelength (295-320 nm)," *Geophys. Res. Lett.* **5**, 191-194 (1978)
- Moortgat, G. E., Kudzus, E., and Warneck, P., "Temperature Dependence of $\text{O}(^1\text{D})$ Formation in the near uv Photolysis of Ozone," *J. Chem. Soc., Faraday Trans. II* **73**, 1216-1221 (1977)

Noertgat, G. K., and Warneck, P., "Relative $G(^1D)$ Quantum Yields in the near UV Photolysis of Ozone at 298 K," *Z. Naturforsch.*, A **30**, 835-844 (1975)

NASA EP-1010. "Chlorofluoromethanes and the Stratosphere"

R. D. Hudson, Editor, August 1977 This reference contains the NASA (1977) rate constant recommendations.

NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA EP 1049 "The Stratosphere: Present and Future," R. D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the June 1979 Harpers Ferry Workshop).

Sparks, R. S., Carson, L., Shobatake, E., Kowalczyk, M. L., and

Lee, Y. T., "Dynamics of Photodissociation of O_3 ," paper

presented at the 7th International Symposium on Molecular Beams, Riva Del Garda, Italy, May 28-June 1, 1975

R. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Photochemical Data

No. Reaction/Reference

9.hv NO + hv -> N + O

NASA (1979) eval

ΔH = 628 kJ/mol; λ_{threshold} = 190 nm

The problem concerning the calculation of the photo-dissociation rate of NO in the upper stratosphere and mesosphere has been re-examined recently by Frederick and Hudson (1979). This problem is closely related to the question of penetration of solar radiation in the Schumann-Runge bands of O₂. Here again the reader is referred to the original publication of Frederick and Hudson.

CODATA (1979) eval

Data sheet on photochemistry of NO

REFERENCES

CODATA(1979). Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.

Frederick, J. E. and Hudson, R. D., "Predissociation of Nitric Oxide in the Mesosphere and Stratosphere," J. Atmos. Sci. **36**, 737-745 (1979)

NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA SP 1049 "The Stratosphere: Present and Future," R. D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the June 1979 Harpers Ferry Workshop).

R. F. Hampson
 June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

No. Reaction/Reference Photochemical Data

10, hv $\text{NO}_2 + \text{hv} \rightarrow \text{NO} + \text{O}$ $\Delta H = 300 \text{ kJ/mol}; \lambda_{\text{threshold}} = 398 \text{ nm}$

NASA (1979) eval

Quantum yields

| λ/nm | ϕ | λ/nm | ϕ |
|---------------------|--------|---------------------|--------|
| 376 | .75 | 396 | .78 |
| 378 | .74 | 398 | .72 |
| 380 | .81 | 400 | .65 |
| 382 | .65 | 402 | .57 |
| 384 | .66 | 404 | .40 |
| 386 | .74 | 406 | .30 |
| 388 | .76 | 408 | .18 |
| 390 | .74 | 410 | .14 |
| 392 | .73 | 415 | .067 |
| 394 | .83 | 420 | .023 |

Absorption cross sections

| λ/nm | $10^{20} \sigma$ | λ/nm | $10^{20} \sigma$ |
|---------------------|------------------|---------------------|------------------|
| 190 | 2.93 | 310 | 1.76 |
| 200 | 2.50 | 320 | 2.54 |
| 210 | 3.85 | 330 | 2.55 |
| 220 | 3.56 | 340 | 3.88 |
| 230 | 2.43 | 350 | 4.10 |
| 240 | .67 | 360 | 4.51 |
| 250 | .28 | 370 | 5.42 |
| 260 | .15 | 380 | 5.55 |
| 270 | .31 | 390 | 6.00 |
| 280 | .55 | 400 | 6.76 |
| 290 | .82 | 410 | 5.77 |
| 300 | 1.17 | | |

CODATA (1979) eval

Detailed data sheet: tabulated values of ϕ and σ

Barker et al (1977) have reported measurements of absorption cross sections and quantum yields in the 375-420 nm region. Their cross sections are 4-10% larger than the values reported by Bass et al (1976), and their quantum yields are, on the average, about 15% smaller than those measured by Jones and Bayes (1973). These two earlier sets of data were the basis for the NBS SP 513 and NASA RP-1010 recommendations. Recent measurements of the quantum yields by Davenport (1978) at six different

wavelengths agree very well with those of Barker et al. The recommended quantum yield values tabulated here, are from Barker et al (1977). The recommended temperature dependent cross values, tabulated here for 298K, are from Bass et al (1976). Davenport's results indicate that the quantum yields themselves are temperature dependent, although the effect of temperature on the cross sections is more pronounced. Uncertainty factor for photochemical rate is 1.25

REFERENCES

- Bass, A. M., Ledford, A. E., Jr., and Laufer, A. E., "Extinction Coefficients of NO_2 and N_2O_4 ," J. Res. Nat. Bur. Stand., Sect. A **80**, 143-166 (1976)
- CCDATA(1979), Recommendations of the CCDAIA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.
- Davenport, J. E., "Determination of NO_2 Photolysis Parameters for Stratospheric Modeling," Report No. FAA-NO-78-14, prepared for U.S. Department of Transportation, Federal Aviation Administration, (1978)
- Hampson, R. F., and Garvin, D., "Reaction Rate and Photochemical Data for Atmospheric Chemistry-1977" U.S. National Bureau of Standards Special Publication 513, May 1978.
- Barker, A. E., Eisele, W., and Rizzo, J. J., "Photodissociation Quantum Yield of NO_2 in the Region 375 to 420 nm," Chem. Phys. Lett. **50**, 394-397 (1977)
- Jones, I. G., and Naylor, K. D., "Photolysis of Nitrogen Dioxide," J. Chem. Phys. **59**, 4836-4844 (1973)
- NASA RP-1010, "Chlorofluoromethanes and the Stratosphere" R. D. Hudson, Editor, August 1977 This reference contains the NASA (1977) rate constant recommendations.
- NASA (1979), Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," R. D. Hudson and E. L. Reed, Editors, Dec. 1979 (report of the June 1979 Harpers Ferry Workshop).
- R. F. Hampson
June 1979

DeMore, W. B., Stief, L. J., Kaufman, F., Golden, D. M., Hampson, R. F.,
Kurylo, M. J., Mergitan, J. J., Molina, M. J., and Watson, R. I.,
"Chemical Kinetic and Photochemical Data for use in Stratospheric
Modelling," JPL Publication 79-27, Jet Propulsion Laboratory,
California Institute of Technology, Pasadena, California, 1979.
Graham, R. A., and Johnston, R. B., "The Photochemistry of NO₃ and the
Kinetics of the N₂O₅-O₃ System," J. Phys. Chem. 82, 254-268 (1978)
Wayne, R. P., Mitchell, D. M., Harrison, R. P., and Allen, R. J.,
1978, 13th Informal Conference on Photochemistry, Clear-
water Beach, Florida, January 4-7.

R. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Photochemical Data |
|-------|--|---|
| 13.4v | $N_2O \xrightarrow{h\nu} N_2 + O(^1D)$ | $\Delta H = 351 \text{ kJ/mol}; \lambda_{\text{threshold}} = 341 \text{ nm}$ |
| | NASA (1979) eval | The recommended cross section values are those of Selwyn et al (1977), who measured the temperature dependence of the absorption cross sections in the atmospherically relevant wavelength regions. They have fitted their data for $\lambda = 173\text{-}240 \text{ nm}$ and $1 - 194\text{-}302 \text{ K}$ with the following expression: |
| | | $\ln \sigma(\lambda, T) = A_1 + A_2\lambda + A_3\lambda^2 + A_4\lambda^3 + A_5\lambda^4$ $+ (T-300)\exp(B_1 + B_2\lambda + B_3\lambda^2 + B_4\lambda^3)$ |
| | | Where T: temperature, Kelvin λ : nm |
| | | $A_1 = 68.21023$ $A_2 = -4.071805$ $A_3 = 4.301146 \times 10^{-2}$ $A_4 = -1.777846 \times 10^{-4}$ $A_5 = 2.520672 \times 10^{-7}$ $B = 1 \quad 185\text{-}\lambda\text{-}230 \text{ nm}$ $B_1 = 123.4014$ $B_2 = -2.116255$ $B_3 = 1.111572 \times 10^{-2}$ $B_4 = -1.881058 \times 10^{-5}$ |
| | CODATA (1979) eval | |

REFERENCES

- CODATA(1979). Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.
- NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," R. D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the June 1979 Harpers Ferry Workshop).
- Selwyn, G., Podolske, J., and Johnston, H. S., "Nitrous Oxide Ultraviolet Absorption Spectrum at Stratospheric Temperatures," Geophys. Res. Lett., **3**, 427-430 (1977)
- R. F. Hampson
 June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Photochemical Data |
|-----|--------------------|--------------------|
|-----|--------------------|--------------------|

| | | |
|--------|--|--|
| 14. hv | $\text{H}_2\text{O}_2 \rightarrow \text{hv} \rightarrow \text{HO}_2 \cdot + \text{HO}_2 \cdot$ $\rightarrow \text{H}_2\text{O}_4 \cdot \cdot$ | $\Delta E = 89 \text{ kJ/mol}; \lambda_{\text{threshold}} = 1340 \text{ nm}$ $\Delta E = 242 \text{ kJ/mol}; \lambda_{\text{threshold}} = 495 \text{ nm}$ |
|--------|--|--|

| NASA (1979) eval | | | |
|---------------------------|---------------------|---------------------|---------------------|
| Absorption cross sections | | | |
| λ/nm | 10^{20} g | λ/nm | 10^{20} g |
| 210 | 520 | 300 | 3.2 |
| 220 | 206 | 310 | 1.5 |
| 230 | 93 | 320 | .75 |
| 240 | 57 | 330 | .40 |
| 250 | 35 | 340 | .27 |
| 260 | 21.2 | 350 | .12 |
| 270 | 15.2 | 360 | .10 |
| 280 | 10.7 | 370 | .05 |
| 290 | 6.3 | 380 | .01 |

CODATA (1979) eval Detailed data sheet on photochemistry of H_2O_2

The cross section values listed here are taken from Graham and Johnston (1978). They supersede the values given in Johnston and Graham (1974). The products and quantum yields are not known.

REFERENCES

- CODATA(1979). Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.
- Graham, R. A., and Johnston, R. S., "The Photochemistry of NO_2 and the Kinetics of the H_2O_2 - O_3 System," J. Phys. Chem. **82**, 254-262 (1978)
- Johnston, R. S., and Graham, R., "Photochemistry of NO_2 and HO_2 Compounds," Can. J. Chem. **52**, 1415-1423 (1974)
- NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future."
- R. D. Hudson and E. L. Reed, Editors, Dec. 1979 (report of the June 1975 Harpers Ferry Workshop).
- B. F. Hampson
 June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

No. Reaction/Reference Photochemical Data

23, hv $H_2O_2 \xrightarrow{h\nu} HO \cdot + HO \cdot$ $\Delta H = 207 \text{ kJ/mol}; \lambda_{\text{threshold}} \approx 578 \text{ nm}$

NASA (1979) eval

Absorption cross sections

| λ/nm | $10^{20} \sigma$ | λ/nm | $10^{20} \sigma$ |
|---------------------|------------------|---------------------|------------------|
| 210 | 37.3 | 290 | 1.2 |
| 220 | 27.0 | 300 | 0.71 |
| 230 | 19.2 | 310 | 0.42 |
| 240 | 13.2 | 320 | 0.24 |
| 250 | 9.0 | 330 | 0.15 |
| 260 | 5.6 | 340 | 0.05 |
| 270 | 3.5 | 350 | 0.05 |
| 280 | 2.1 | | |

CODATA (1979) eval

$\beta = 1$ $200 < \lambda < 350 \text{ nm}$

There are now two measurements of the absorption cross sections of H_2O_2 vapor in the 300 nm region (Molina et al (1977) and Lin et al (1978)). The recommended values are the mean of the two sets of data. Uncertainty factor for photochemical rate is 1.4

REFERENCES

CODATA(1979). Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.

Lin, C. L., Rohatgi, N. K., and DeMore, W. B., "Ultraviolet Absorption Cross Sections of Hydrogen Peroxide," *Geophys. Res. Lett.* **5**, 113-115 (1978)

Molina, L. T., Schinke, R. D., and Molina, M. J., "Ultraviolet Absorption Spectrum of Hydrogen Peroxide Vapor," *Geophys. Res. Lett.* **4**, 580-582 (1977)

NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," R. D. Hudson and E. L. Reed, Editors, Dec. 1979 (report of the June 1979 Barpers Ferry Workshop).

R. F. Hampson
 June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

No. Reaction/Reference Photochemical Data

25, hv $\text{HNO}_2 \xrightarrow{\text{hv}} \text{HO} + \text{NO}$ $\Delta H = 202 \text{ kJ/mol}$; $\lambda_{\text{threshold}} = 590 \text{ nm}$

NASA (1979) eval

Absorption cross sections

| λ/nm | $10^{20} \sigma$ | λ/nm | $10^{20} \sigma$ |
|---------------------|------------------|---------------------|------------------|
| 310 | 0.0 | 355 | 24.6 |
| 315 | 0.4 | 360 | 6.8 |
| 320 | 2.1 | 365 | 13.2 |
| 325 | 4.0 | 370 | 11.5 |
| 330 | 7.3 | 375 | 2.7 |
| 335 | 6.4 | 380 | 7.8 |
| 340 | 10.5 | 385 | 19.0 |
| 345 | 8.5 | 390 | 1.2 |
| 350 | 6.8 | 395 | 0.0 |

CODATA (1979) eval

$\sigma = 1 \text{ } 300 < \lambda < 400 \text{ nm}$

Also tabulated values of σ averaged over 5 nm intervals

The ultraviolet spectrum of HONO between 300 and 400 nm has been studied recently by Stockwell and Calvert (1978) by examination of its equilibrium mixtures with NO , NO_2 , H_2O , N_2O and N_2O_4 ; the possible interferences by these compounds were taken into account. The cross section values given here at 5 nm intervals are taken from the extensive table of preferred cross section values tabulated at 1 nm intervals in that reference. No recommendation is given for the 200-300 nm range. Uncertainty factor for photochemical rate is 1.4

REFERENCES

CODATA(1979). Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.

NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," R. D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the June 1979 Harpers Ferry Workshop).

Stockwell, W. R., and Calvert, J. G., "The Near Ultraviolet Absorption Spectrum of Gaseous HONO and N_2O_3 ," J. Photochem. **5**, 153-203 (1978)

R. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Photochemical Data

No. Reaction/Reference

26. hv $\text{HNO}_3 \rightarrow \text{H}\cdot + \text{H}\cdot + \text{NO}_2$ $\Delta H = 200 \text{ kJ/mol}$; $\lambda_{\text{threshold}} = 598 \text{ nm}$

CODATA (1979) eval

Absorption cross sections

| λ/nm | $10^{20} \sigma$ | λ/nm | $10^{20} \sigma$ |
|---------------------|------------------|---------------------|------------------|
| 190 | 1320 | 260 | 1.50 |
| 200 | 550 | 270 | 1.63 |
| 210 | 97 | 280 | 1.14 |
| 220 | 14.4 | 290 | 0.63 |
| 230 | 5.6 | 300 | 0.28 |
| 240 | 2.6 | 310 | 0.05 |
| 250 | 1.5 | 320 | 0.02 |

$\beta = 1$ $190 < \lambda < 320 \text{ nm}$

The recommended cross section values are those of Johnston and Graham (1973). The recommended quantum yield is based on result of Johnston et al (1974). Uncertainty factor for photochemical rate is 1.2

REFERENCES

- CODATA(1979). Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.
- Johnston, H. S., Chang, S.-G., and Whitten, G., "Photolysis of Nitric Acid Vapor," J. Phys. Chem. **78**, 1-7 (1974)
- Johnston, H. S., and Graham, R., "Gas Phase Ultraviolet Absorption Spectrum of Nitric Acid Vapor," J. Phys. Chem. **77**, 62-63 (1973)
- H. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

No. Reaction/Reference

Photochemical Data

26a. hv \rightarrow products
NASA (1979) eval

| Absorption cross sections | | | |
|---------------------------|--------------------------|---------------------|--------------------------|
| λ/nm | 10^{20} s^{-1} | λ/nm | 10^{20} s^{-1} |
| 150 | 1610 | 270 | 28 |
| 200 | 640 | 280 | 18 |
| 210 | 250 | 290 | 10.9 |
| 220 | 154 | 300 | 6.2 |
| 230 | 95 | 310 | 4.2 |
| 240 | 62 | 320 | 3.0 |
| 250 | 51 | 330 | 2.2 |
| 260 | 40 | | |

CODATA (1979) eval

Detailed data sheet on photochemistry of H_2NO_2

Two groups have investigated the UV spectrum of H_2NO_2 : Graham et al (1978) and Cox and Patrick (1979). Only the former reports cross section values in the critical wavelength region for atmospheric photo-dissociation beyond 250 nm. The results of Graham et al, which provides the basis of this recommendation, are listed here. The two sets of results are in reasonable agreement between 205 and 260 nm, but at 195 nm the cross-section value obtained by Graham et al is more than twice the value reported by Cox and Patrick. Additional studies of the H_2NO_2 spectrum would be desirable.

REFERENCES

CODATA(1979). Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.

Cox, R. A., and Patrick, R., "Kinetics at the Reaction of $\text{H}_2 + \text{NO}_2(\text{M}) + \text{H}_2\text{NO}_2$ using Molecular Modulation Spectrometry. Int. J. Chem. Kinet., **11**, 635-648 (1979)

Graham, R. A., Winer, A. M., and Pitts, J. N. Jr., "Ultraviolet and Infrared Absorption Cross Sections of Gas Phase H_2NO_2 ." Geophys. Res. Lett., **11**, 909-911 (1978)

NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA EP 1049 "The Stratosphere: Present and Future." R. D. Hudson and E. L. Reed, Editors, Dec. 1975 (report of the June 1975 Harpers Ferry Workshop).

R. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Photochemical Data |
|-------|---|---|
| 28,hv | SO ₂ + hv → products NASA (1979) eval | The photodissociation of SO ₂ in the atmosphere as well as the potential role of excited states of SO ₂ in atmospheric chemistry has been reviewed recently by Calvert et al (1978) and will not be repeated here |

REFERENCES

- Calvert, J. G., Su, F., Bottenheim, J. W., and Strausz, G. P.,
"Mechanism of the Homogeneous Oxidation of Sulfur Dioxide in
the Troposphere," Atmos. Environ. 12, 197 (1978)
- NASA (1979). Recommendations of the NASA Panel for Data Evaluation,
published in NASA RP 1049 "The Stratosphere: Present and Future,"
E. D. Hudson and E. I. Reed, Editors, Dec. 1975 (report of the
June 1975 Harpers Ferry Workshop).
- E. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Photochemical Data | | |
|--------|--|--|--|------|
| | | ΔH° kJ/mol; $\lambda_{\text{threshold}}^\circ$ nm | Absorption cross sections | |
| 340.44 | C6S + hv -> C6 + S NASA (1979) eval | λ_{max} | $10^{20} \text{ cm}^2 \text{ mol}^{-1} \text{ s}^{-1}$ | |
| | | | 232K | 296K |
| | | 186.0 | 9.8 | 10.6 |
| | | 187.8 | 5.6 | 6.6 |
| | | 189.6 | 2.0 | 2.5 |
| | | 191.4 | 1.0 | 1.3 |
| | | 193.2 | 0.9 | 1.1 |
| | | 195.1 | 1.2 | 1.5 |
| | | 197.0 | 1.9 | 2.1 |
| | | 199.0 | 2.7 | 2.9 |
| | | 201.0 | 3.7 | 4.0 |
| | | 203.0 | 5.2 | 5.4 |
| | | 205.1 | 7.0 | 7.2 |
| | | 207.3 | 9.3 | 9.9 |
| | | 209.4 | 12.0 | 12.1 |
| | | 211.6 | 16.0 | 16.1 |
| | | 213.9 | 19.9 | 20.1 |
| | | 216.2 | 22.8 | 23.1 |
| | | 218.6 | 24.5 | 24.9 |
| | | 221.0 | 26.7 | 26.9 |
| | | 223.5 | 29.1 | 29.5 |
| | | 226.0 | 27.3 | 28.0 |

The recommended cross section values, listed here are those measured as a function of temperature by Chou et al (1975). Their room temperature results agree within 2% with the values reported earlier by Breckenridge and Taube (1970). The photodissociation quantum yields have not been measured yet in the atmospherically important wavelength region around 200 nm, although they are likely to be unity. The results of Elenk et al (1975) indicate that oxygen atoms are not formed in the photodissociation of C6S; C6 and S are the only products. The uncertainty factor for the photochemical rate is 1.25

REFERENCES

Breckenridge, W. E., and Taube, H., "Ultraviolet Absorption Spectrum of Carbonyl Sulfide," J. Chem. Phys. 52, 1713-1715 (1970)

Chou, C. C., Ruiz, E. V., and Rowland, F. S., to be published in *Geophysics Research Letters* (1979)

Klemm, E. B., Glicker, S., and Stief, L. J., "Relative Quantum Yield for the Production of O-Atoms and H-Atom from the Photodissociation of OCS in the Vacuum UV," *Chem. Phys. Lett.* 23, 512-517 (1975)

NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," E. D. Hudson and E. L. Reed, Editors, Dec. 1979 (report of the June 1975 Harpers Ferry Workshop).

E. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Photochemical Data |
|------------|--|--|
| 36, hv | ClO + hv - Cl + O | <p>ΔH = 264 kJ/mol; λ_{threshold} = 453 nm</p> |
| | NASA (1979) eval | <p>There are new measurements of ClO absorption cross sections in the 270-312 nm region, by Jourdain, et al (1978). Earlier absorption cross section data have been reviewed by Watson (1977). Two recent calculations (Langhoff et al, 1977; and Coxon et al, 1976) indicate that photodecomposition (predissociation of the A²Π_{3/2} state) of ClO accounts for at most 2 to 3 percent of the total destruction rate of ClO in the stratosphere, which occurs predominantly by reaction with oxygen atoms and nitric oxide</p> |
| REFERENCES | | |
| | | |
| | Coxon, J. A., Jones, W. E., and Ramsey, D. A., 12th International Symposium on Free Radicals, Laguna Beach, California, (1976) | |
| | Jourdain, J. L., LeBras, G., Poulet, G., Combourieu, J., Bigaud, P., and Laloy, B., "UV Absorption Spectrum of ClO(A ² Π-X ² Π) up to the (1,0) Band," Chem. Phys. Lett. 57, 109-112 (1978) | |
| | Langhoff, S. E., Jaffe, E. L., and Arnold, J. G., "Effective Cross Sections and Rate Constants for Predissociation of ClO in the Earth's Atmosphere," J. Quant. Spectrosc. Radiat. Transfer 18, 227-235 (1977) | |
| | NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA EP 1049 "The Stratosphere: Present and Future," E. D. Hudson and E. L. Reed, Editors, Dec. 1979 (report of the June 1979 Harpers Ferry Workshop) | |
| | Watson, E. L., "Rate Constants for Reactions of ClO ₂ of Atmospheric Interest," J. Phys. Chem. Ref. Data 6, 871-918 (1977) | |
| | E. F. Hampson June 1979 | |

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Photochemical Data |
|----------------------------------|---|--|
| 37, hv | $\text{ClO} + \text{hv} \rightarrow \text{Cl} + \text{O}(\text{}^3\text{P})$ $\quad \quad \quad \rightarrow \text{Cl} + \text{O}(\text{}^1\text{D})$ | $\Delta H = 252 \text{ kJ/mol}; \lambda_{\text{threshold}} = 464 \text{ nm}$ $\Delta H = 448 \text{ kJ/mol}; \lambda_{\text{threshold}} = 267 \text{ nm}$ |
| Watson (1977) review | | |
| Absorption cross sections | | |
| λ/nm | $10^{15} \text{ } \sigma$ | |
| 225 | 2.6 | |
| 235 | 7.8 | |
| 245 | 12.7 | |
| 255 | 12.4 | |
| 265 | 7.3 | |
| 275 | 3.4 | |

REFERENCES

Watson, R. L., "Rate Constants for Reactions of ClO_2 of Atmospheric Interest," J. Phys. Chem. Ref. Data **6**, 871-918 (1977)

R. F. Hampson
 May 1978

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Photochemical Data | | | |
|-------------------------------|--|--|--|------------------------------|---------------------|
| | | ΔH | $\lambda_{\text{threshold}}$ | $\lambda_{\text{threshold}}$ | |
| 37, hv | $\text{OCl}_2 \xrightarrow{h\nu} \text{Cl} + \text{Cl} \cdot \text{O}(\text{Cl})$ $\text{OCl}_2 \xrightarrow{h\nu} \text{Cl} + \text{Cl} \cdot \text{O}(\text{Cl})$ | $\Delta H = 249 \text{ kJ/mol}$ $\Delta H = 439 \text{ kJ/mol}$ | $\lambda_{\text{threshold}} = 460 \text{ nm}$ $\lambda_{\text{threshold}} = 272 \text{ nm}$ | | |
| Watson (1977) review | | | | | |
| Absorption cross section data | | | | | |
| | | λ/nm | 10^{20} g | λ/nm | 10^{20} g |
| | | 476 | 0.54 | 183 | 360 |
| | | 469 | 0.80 | 163 | 1420 |
| | | 460 | 0.74 | 160 | 1100 |
| | | 454 | 5.8 | 153 | 1150 |
| | | 446 | 34.0 | 152 | 1110 |
| | | 440 | 26.5 | 151 | 1070 |
| | | 351 | 1140 | 150 | 688 |

REFERENCES

Watson, R. L., "Rate Constants for Reactions of ClO_2 of Atmospheric Interest," *J. Phys. Chem. Ref. Data* **6**, 871-918 (1977)
 R. L. Hansen
 May 1978

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Photochemical Data

| No. | Reaction/Reference | Absorption cross sections | | | |
|-------|--|---------------------------|--------------------|-----------------------|--------------------|
| | | λ_{nm} | $10^{18} \epsilon$ | λ_{nm} | $10^{18} \epsilon$ |
| 38.3b | ClO ₂ + hv → products NASA (1979) eval | 200 | 5.3 | 280 | 4.6 |
| | | 210 | 5.0 | 290 | 4.3 |
| | | 220 | 4.8 | 300 | 4.0 |
| | | 230 | 4.3 | 310 | 3.2 |
| | | 240 | 3.5 | 320 | 2.5 |
| | | 250 | 3.7 | 330 | 1.8 |
| | | 260 | 4.3 | 340 | 1.1 |
| | | 270 | 4.5 | 350 | 0.76 |
| | | | | | |
| | | | | | |
| | | | | | |
| | | | | | |

These absorption cross sections of chlorine trioxide, ClO₃, for the 200-350 nm range have been obtained by graphical interpolation between the data points of Goodeve and Richardson (1937). Although the quantum yield for decomposition has not been measured, the continuous nature of the spectrum indicates that it is likely to be unity.

REFERENCES

- Goodeve, C. F., and Richardson, F. D., "The Absorption Spectrum of Chlorine Trioxide and Chlorine Peroxide," *Trans. Faraday Soc.* **33**, 453-457 (1937)
- NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future,"
- B. D. Hudson and E. I. Reed, Editors, Dec. 1975 (report of the June 1975 Harpers Ferry Workshop).
- B. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Photochemical Data

$\Delta H = 426 \text{ kJ/mol}$; $\lambda_{\text{threshold}} = 280 \text{ nm}$

Watson (1977) review

Absorption cross sections

| λ/nm | 10^{20} g | λ/nm | 10^{20} g |
|---------------------|---------------------|---------------------|---------------------|
| 140 | 211 | 185 | 31.3 |
| 145 | 281 | 190 | 14.5 |
| 150 | 345 | 195 | 6.18 |
| 155 | 382 | 200 | 2.56 |
| 160 | 332 | 205 | 0.58 |
| 165 | 248 | 210 | 0.39 |
| 170 | 163 | 215 | 0.14 |
| 175 | 105 | 220 | 0.05 |
| 180 | 58.8 | | |

REFERENCES

Watson, R. T., "Rate Constants for Reactions of ClO_2 of Atmospheric Interest," J. Phys. Chem. Ref. Data **6**, 871-918 (1977)

R. F. Hampson
 May 1978

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Photochemical Data |
|--------|---|---|
| 30P,40 | $\text{HF} + \text{h}\nu \rightarrow \text{H} + \text{F}$ NASA (1979) eval | $\Delta H = 567 \text{ kJ/mol}$; $\lambda_{\text{threshold}} = 210 \text{ nm}$ The ultraviolet absorption spectrum of HF has been studied by Safary et al (1951). The onset of absorption occurs beyond 176 nm, so that photodissociation of HF will be unimportant in the stratosphere |

REFERENCES

- NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," E. D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the June 1975 Harpers Ferry Workshop).
- Safary, E., Rosand, J., and Vodar, E., "Ultraviolet Absorption Spectrum of Gaseous Hydrogen Fluoride," J. Chem. Phys. **19**, 375-380 (1951)
- E. F. Hampson
 June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Photochemical Data

No. Reaction/Reference

40. hv HgCl + hv → Hg + Cl

ΔH = 233 kJ/mol; λ_{threshold} = 513 nm

NASA (1979) eval

Absorption cross sections

| λ/nm | 10 ²⁰ σ | λ/nm | 10 ²⁰ σ |
|------|--------------------|------|--------------------|
| 200 | 5.2 | 310 | 6.2 |
| 210 | 6.1 | 320 | 5.0 |
| 220 | 11.0 | 330 | 3.7 |
| 230 | 18.6 | 340 | 2.4 |
| 240 | 22.3 | 350 | 1.4 |
| 250 | 18.0 | 360 | 0.8 |
| 260 | 10.8 | 370 | 0.45 |
| 270 | 6.2 | 380 | 0.24 |
| 280 | 4.8 | 390 | 0.15 |
| 290 | 5.3 | 400 | 0.05 |
| 300 | 6.1 | 420 | 0.04 |

CODATA (1979) eval

Detailed data sheet on photochemistry of HgCl

Knauth et al (1979) have recently measured absorption cross sections of HgCl using essentially the same technique as Molina and Molina (1978) except for a higher temperature, which allowed them to obtain a more accurate value for the equilibrium constant K_{eq} for the H_2O-Cl_2-HgCl system. The cross section values from Molina and Molina's measurements, recalculated using the new K_{eq} , are in excellent agreement with the results of Knauth et al. The recommended values, taken from this later work, are given here. Molina et al (1979a), by monitoring directly OH radicals produced by laser photolysis of HgCl, obtain an absorption cross section value of $\sim 6 \times 10^{-20} \text{ cm}^2$ around 310 nm, again in excellent agreement with the data of Knauth et al (1979). In contrast, the theoretical predictions of Jaffe and Langhoff (1978) indicate negligible absorption at those wavelengths. The reason is not known, although it should be pointed out that no precedent exists to validate the theoretical approach for this particular type of problem.

REFERENCES

CODATA(1979). Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.

- Jaffe, R. L., and Linschott, R. R., "Theoretical Study of the Photodissociation of HCl," *J. Chem. Phys.* **68**, 1638-1646 (1978)
- Knauth, R.-D., Alberti, R., and Clausen, R., "Equilibrium Constant of the Gas Reaction $\text{Cl}_2 + \text{H}_2 \rightarrow 2\text{HCl}$ and the Ultraviolet Spectrum of HCl," *J. Phys. Chem.* **83**, 1608-1612 (1979)
- Meliss, L. T., and Meliss, M. J., "Ultraviolet Spectrum of HCl," *J. Phys. Chem.* **82**, 2410-2414 (1978)
- Meliss, L. T., Ishiwata, T., and Meliss, M. J., "Quantum Yield for Production of OH in the Photolysis of HCl at 310 nm, submitted to *J. Chem. Phys.* 1979a.
- NASA (1979), Recommendations of the NASA Panel for Data Evaluation, published in NASA EP 1049 "The Stratosphere: Present and Future," R. D. Hudson and R. L. Reed, Editors, Dec. 1979 (report of the June 1975 Harpers Ferry Workshop).
- R. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Photochemical Data | | | |
|--------|--|---------------------------|---------------------|---------------------|---------------------|
| | | Absorption cross sections | | | |
| | | λ/nm | 10^{20} g | λ/nm | 10^{20} g |
| 41a,bv | HClO ₄ + hv -> products NASA (1979) eval | 150 | 405 | 240 | 1.4 |
| | | 165 | 230 | 245 | 0.76 |
| | | 200 | 130 | 250 | 0.40 |
| | | 205 | 78 | 255 | 0.21 |
| | | 210 | 45 | 260 | 0.12 |
| | | 215 | 25 | 265 | 0.06 |
| | | 220 | 14 | 270 | 0.03 |
| | | 225 | 8.0 | 275 | 0.02 |
| | | 230 | 4.4 | 280 | 0.01 |
| | | 235 | 2.5 | | |
| | | | | | |
| | | | | | |
| | | | | | |

The results tabulated here are from the study of Molina et al (1975b)

REFERENCES

- Molina, L. G., Hansen, L., Cook, J., and Molina, M. J., "Ultraviolet Absorption Spectrum of HClO₄ Vapor, submitted to J. Photochem. 1979b.
- NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," E. D. Hudson and E. I. Reed, Editors, Dec 1975 (report of the June 1975 Harpers Ferry Workshop).
- E. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS
Photochemical Data

| No. | Reaction/Reference | $\Delta H = 156 \text{ kJ/mol}$; $\lambda_{\text{threshold}} = 765 \text{ nm}$ |
|--------|---|---|
| 42, hv | $\text{NOCl} \cdot \text{hv} \rightarrow \text{Cl} \cdot \text{NO}$ | |
| | NASA (1979) eval | |
| | | Absorption cross sections |
| | λ/nm | 10^{19} g |
| | 150 | 280 |
| | 200 | 300 |
| | 210 | 320 |
| | 220 | 340 |
| | 230 | 360 |
| | 240 | 380 |
| | 260 | 400 |
| | | 10^{15} g |
| | | 0.10 |
| | | 0.55 |
| | | 1.21 |
| | | 1.37 |
| | | 1.22 |
| | | 0.83 |
| | | 0.51 |

Nitrosyl chloride - a green gas - has a continuous absorption extending beyond 650 nm. There is good agreement between the work of Martin and Garelis (1956) for the 240-420 nm wavelength region, of Ballash and Armstrong (1974) for the 185-540 nm region, and of Illies and Takacs (1976) for the 190-400 nm region. These results indicate that the early data of Goodeve and Katz (1935) were seriously in error between 186 and 300 nm, whereas, at longer wavelengths, they are in good agreement with the more recent measurements.

The results of Ballash and Armstrong (1974) and of Illies and Takacs (1976) agree within 20 percent except in the region near 240 nm, where the values of Ballash and Armstrong are about 60 percent higher. The recommended cross sections were obtained by taking the mean of the two studies.

The quantum yield for the primary photolytic process has been reviewed by Calvert and Pitts (1967); it is unity over the entire visible and near-ultraviolet bands.

REFERENCES

- Ballash, M. M., and Armstrong, D. A., "On the Ultraviolet and Visible Absorption Spectrum of ClNO," *Spectrochim. Acta* **30**, A, 541-544 (1974)
- Calvert, J. G., and Pitts, J. N., "Photochemistry," John Wiley & Sons, Inc., New York, p. 230-231 (1967)
- Goodeve, C. F., and Katz, S., "The Absorption Spectrum of Nitrosyl Chloride," *Proc. Roy. Soc. (London)* **A 172**, 432-444 (1939)

111100. As J. and Tabata, G. A. "Gas Phase Ultra-Violet
Photoabsorption Cross-Sections for Nitrosyl Chloride and
Nitryl Chloride," J. Photochem. 6, 35-42 (1976)

Cartin, R., and Gareis, R. "Die Kinetik der Reaktion von
ClO₂ mit NO₂ in der Lösungsphase," Z. Elektrochem.
69, 959-964 (1965)

NASA (1979). Recommendations of the NASA Panel for Data Evaluation.
Published in NASA RP 1049 "The Stratosphere: Present and Future."
P. D. Hudson and E. I. Reed, Editors. Dec. 1979 (report of the
June 1979 Harpers Ferry Workshop).

P. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Photochemical Data

| No. | Reaction/Reference | Absorption cross sections | | | |
|--------|--|---------------------------|-----------------------------|---------------------|-----------------------------|
| | | λ/nm | $10^{20} \text{ } \epsilon$ | λ/nm | $10^{20} \text{ } \epsilon$ |
| 43, 44 | $\text{ClNO}_2 \xrightarrow{h\nu} \text{products}$ | 150 | 2690 | 300 | 15.4 |
| | | 200 | 455 | 310 | 13.2 |
| | | 210 | 339 | 320 | 10.2 |
| | | 220 | 342 | 330 | 7.11 |
| | | 230 | 236 | 340 | 4.81 |
| | | 240 | 140 | 350 | 3.06 |
| | | 250 | 98.5 | 360 | 1.82 |
| | | 260 | 63.7 | 370 | 1.07 |
| | | 270 | 37.3 | 380 | 0.63 |
| | | 280 | 23.1 | 390 | 0.38 |
| | | 290 | 18.0 | 400 | 0.21 |

NASA (1979) eval

The absorption cross sections of nitryl chloride, ClNO_2 , have been measured between 230 and 330 nm by Martin and Garcia (1956) and between 185 and 400 nm by Illies and Takacs (1976). The results are in good agreement. The recommended cross sections are taken from Illies and Takacs (1976).

The photochemistry of ClNO_2 has not yet been studied. Likely photolysis products are Cl and NO_2 , and the quantum yield for decomposition is probably unity, due to the characteristics of the spectrum.

REFERENCES

- Illies, A. J., and Takacs, G. A., "Gas Phase Ultra-Violet Photoabsorption Cross-Sections for Nitroxy Chloride and Nitryl Chloride," *J. Photochem. Sci.*, 35-42 (1976)
- Martin, E., and Garcia, E., "Die Kinetik der Reaktion von ClO_2 mit NO_2 in der Lösungssphase," *Z. Elektrochem.*, 59, 559-564 (1956)

NASA (1979). Recommendations of the NASA Panel for Data Evaluation,
published in NASA EP 1049 "The Stratosphere: Present and Future."
E. D. Hudson and E. I. Reed, Editors. Dec. 1979 (report of the
June 1979 Harpers Ferry Workshop).

E. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Photochemical Data | | | |
|--------|---|--------------------|-------------|------------------------------------|-------------|
| | | λ_{max} | $10^{20} g$ | λ_{max} | $10^{20} g$ |
| 43, hv | ClONO + hv \rightarrow products NASA (1979) eval | | | Absorption cross sections at 231 Å | |
| | | 225 | 215.0 | 320 | 80.3 |
| | | 240 | 176.0 | 325 | 75.4 |
| | | 245 | 137.0 | 330 | 58.7 |
| | | 250 | 106.0 | 335 | 57.7 |
| | | 255 | 65.0 | 340 | 43.7 |
| | | 260 | 64.6 | 345 | 35.7 |
| | | 265 | 65.3 | 350 | 26.5 |
| | | 270 | 90.3 | 355 | 22.9 |
| | | 275 | 110.0 | 360 | 16.1 |
| | | 280 | 132.0 | 365 | 11.3 |
| | | 285 | 144.0 | 370 | 5.0 |
| | | 290 | 144.0 | 375 | 6.5 |
| | | 295 | 142.0 | 380 | 4.1 |
| | | 300 | 129.0 | 385 | 3.3 |
| | | 305 | 114.0 | 390 | 2.2 |
| | | 310 | 105.0 | 395 | 1.5 |
| | | 315 | 98.1 | 400 | 0.6 |

Measurements in the near-ultraviolet of the cross sections at 231 Å of chlorine nitrite (ClONO) have been made by Molina and Molina (1977). Their results are given here. The characteristics of the spectrum and the instability of ClONO strongly suggest that the quantum yield for decomposition is unity. The Cl-O bond strength is only about 80 kJ so that chlorine atoms are likely photolysis products.

REFERENCES

- Molina, L. T., and Molina, M. J., "Ultraviolet Absorption Spectrum of Chlorine Nitrite, ClONO," *Geophys. Res. Lett.* **4**, 23-26 (1977)
- NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," P. D. Hudson and E. L. Reed, Editors, Dec. 1979 (report of the June 1979 Harpers Ferry Workshop).

P. F. Hampson
 June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Photochemical Data | | | | | |
|-----------------------|--|---------------------------|-------|--------------------|------|-------|-------|
| | | Absorption cross sections | | | | | |
| λ ₃₀₀ , mμ | NO ₂ Cl + hv → products NASA (1979) eval | λ/μm | | 10 ²⁰ σ | | λ/μm | |
| | | 227K | 296K | 227K | 296K | 227K | 296K |
| | | 150 | 555 | 589 | 330 | 0.353 | 0.514 |
| | | 200 | 293 | 307 | 340 | 0.246 | 0.323 |
| | | 210 | 330 | 329 | 350 | 0.198 | 0.246 |
| | | 220 | 348 | 344 | 360 | 0.170 | 0.208 |
| | | 230 | 206 | 210 | 370 | 0.142 | 0.162 |
| | | 240 | 98.5 | 106 | 380 | 0.113 | 0.122 |
| | | 250 | 52.6 | 57.7 | 390 | 0.090 | 0.050 |
| | | 260 | 30.7 | 34.6 | 400 | 0.056 | 0.064 |
| | | 270 | 18.3 | 21.5 | 410 | - | 0.044 |
| | | 280 | 10.4 | 11.9 | 420 | - | 0.027 |
| | | 290 | 5.45 | 6.36 | 430 | - | 0.016 |
| | | 300 | 2.51 | 3.30 | 440 | - | 0.009 |
| | | 310 | 1.28 | 1.69 | 450 | - | 0.005 |
| | | 320 | 0.630 | 0.895 | | | |

CODATA (1979) eval

Detailed data sheet on photochemistry of ClONO₂

The cross sections recommended in NASA RP 1010 were based on measurements by Rowland, Spencer and Molina (1976). Molina and Molina (1979) carried out new measurements using essentially the same technique but under conditions of higher sensitivity (a longer absorption path), and as a function of temperature. Their room temperature values are ~ 15% lower than the earlier measurements. The recommended values listed here are taken from the newer study. The identity of the primary photolytic fragments has been investigated by two groups: Smith et al (1977) report O + ClONO₂ as the most likely products, using end product analysis and steady-state photolysis, whereas the results of Chang et al (1979), who employed the "Very Low Pressure Photolysis" (VLPPh) technique, indicate that the products are Cl + NO₂. In view of the more direct nature of the VLPPh technique these later results are preferred. Uncertainty factor for photochemical rate is 1.25.

REFERENCES

- Chang, J. S., Barker, J. R., Davenport, J. R., and Golden, D. M., "Chlorine Nitrate Photolysis by a new Technique: Very Low Pressure Photolysis," Chem. Phys. Lett. **50**, 385-390 (1979)

COBATA(1979). Recommendations of the COBATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.

Molina, L. J., and Molina, M. J., "Chlorine Nitrate Ultraviolet Absorption Spectrum at Stratospheric Temperatures," J. Photochem. 11, 139-144 (1979)

Bowland, F. S., Spencer, J. E., and Molina, M. J., "Stratospheric Formation and Photolysis of Chlorine Nitrate," J. Phys. Chem. 80, 2711-2713 (1976)

Smith, W. S., Chou, C. C., and Bowland, F. S., "The Mechanism for Ultraviolet Photolysis of Gaseous Chlorine Nitrate at 302.5 nm," Geophys. Res. Lett. 4, 517-519 (1977)

E. F. Hansen
June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Photochemical Data

No. Reaction/Reference

43a.Br.hv BrONO₂ → hv → Products
 NASA (1979) eval

| Absorption cross sections | | | |
|---------------------------|---------------------|---------------------|---------------------|
| λ/nm | 10^{20} s | λ/nm | 10^{20} s |
| 150 | 1300 | 300 | 15 |
| 200 | 720 | 310 | 15 |
| 210 | 320 | 320 | 12 |
| 220 | 240 | 330 | 10 |
| 230 | 190 | 340 | 6.7 |
| 240 | 130 | 350 | 7.7 |
| 250 | 78 | 360 | 6.2 |
| 260 | 48 | 370 | 4.9 |
| 270 | 34 | 380 | 4.0 |
| 280 | 25 | 390 | 2.8 |
| 290 | 24 | | |

CODATA (1979) eval

Detailed data sheet on photochemistry of BrONO₂

The bromine nitrate cross sections have been measured at room temperature by Spencer and Rowland (1978) in the wavelength region 186-390 nm. The recommended values are given here. By analogy with ClONO₂, some temperature dependence may be expected. The photolysis products are not known. The uncertainty factor for the photochemical rate is 1.4

REFERENCES

- CODATA(1979). Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.
- NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA EP 1049 "The Stratosphere: Present and Future," E. D. Hudson and E. L. Reed, Editors, Dec. 1975 (report of the June 1975 Harpers Ferry Workshop).
- Spencer, J. E., and Rowland, F. S., "Bromine Nitrate and its Stratospheric Significance," J. Phys. Chem. **82**, 7-10 (1978)
- E. F. Hampson
 June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Photochemical Data

No. Reaction/Reference

44.4v $\text{Cl}_2 + h\nu \rightarrow \text{Cl} + \text{Cl}$

$\Delta H = 240 \text{ kJ/mol}$; $\lambda_{\text{threshold}} = 500 \text{ nm}$

Watson (1977) review

Absorption cross-sections

| λ/nm | $10^{21} \sigma$ |
|---------------------|------------------|
| 240 | 0.2 |
| 260 | 2.3 |
| 280 | 27 |
| 300 | 120 |
| 320 | 236 |
| 340 | 236 |
| 360 | 131 |
| 380 | 49 |
| 400 | 19 |
| 420 | 9.9 |
| 440 | 5.3 |

REFERENCES

Watson, R. L., "Rate Constants for Reactions of ClO_2 of Atmospheric Interest," J. Phys. Chem. Ref. Data **6**, 871-918 (1977)

R. F. Hampson
 May 1978

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Photochemical Data | | | | |
|-------|---|--|-------------------------|----------|----------|--|
| 48.46 | $CH_2O + h\nu \rightarrow H + CO$ (1) $\rightarrow H_2 + CO$ (2) CODATA (1979) eval | $\Delta H = 358$ kJ/mol; λ threshold = 334 nm | | | | |
| | | $\Delta H = -9$ kJ/mol | | | | |
| | | Absorption cross sections and quantum yields for 300%, 1 atm air | | | | |
| | | λ/nm | 10^{-20} cm^2 | ϕ_1 | ϕ_2 | |
| | | 280 | 2.4 | 0.63 | 0.37 | |
| | | 290 | 3.2 | 0.73 | 0.27 | |
| | | 300 | 3.3 | 0.77 | 0.23 | |
| | | 310 | 3.1 | 0.76 | 0.24 | |
| | | 320 | 2.4 | 0.63 | 0.37 | |
| | | 330 | 2.4 | 0.31 | 0.64 | |
| | | 340 | 2.0 | 0 | 0.67 | |
| | | 350 | 0.8 | 0 | 0.40 | |
| | 360 | 0.2 | 0 | 0.14 | | |

These recommendations accepted for NASA (1975) evaluation

REFERENCES

CODATA(1979). Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.

NASA (1979). Recommendations of the NASA Panel for Data Evaluation. published in NASA EP 1049 "The Stratosphere: Present and Future." R. D. Hudson and R. L. Reed, Editors, Dec. 1979 (report of the June 1979 Harpers Ferry Workshop).

R. F. Hampson
 June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Photochemical Data | | | |
|-------|--|------------------------|--------------------|------------------------|--------------------|
| | | λ_{max} | $10^{20} \epsilon$ | λ_{min} | $10^{20} \epsilon$ |
| 53.3b | CH ₃ OH + hv → products NASA (1979) eval | 210 | 37.5 | 290 | 0.90 |
| | | 220 | 22.0 | 300 | 0.52 |
| | | 230 | 13.6 | 310 | 0.34 |
| | | 240 | 8.6 | 320 | 0.19 |
| | | 250 | 5.6 | 330 | 0.11 |
| | | 260 | 3.8 | 340 | 0.06 |
| | | 270 | 2.6 | 350 | 0.04 |
| | | 280 | 1.5 | | |
| | | | | | |
| | | | | | |

Molina and Arguello (1979) have measured the absorption cross sections of CH₃OH. Their results are given here. The uncertainty factor for the photochemical rate is 1.4

REFERENCES

- Molina, M. J., and Arguello, G., "Ultraviolet Absorption Spectrum of Methylhydroperoxide Vapor," *Geophya. Res. Lett.* **A. 953-955** (1979)
- NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA SP 1049 "The Stratosphere: Present and Future."
- R. D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the June 1979 Harpers Ferry Workshop).

R. F. Hampson
 June 1979

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

| No. | Reaction/Reference | Photochemical Data |
|--------|--|--|
| 54, hv | $\text{CH}_3\text{CHO} + \text{h}\nu \rightarrow \text{CH}_3\dot{\text{C}}\text{H} + \text{H}\dot{\text{C}}\text{O}$ (a) - isomer (b) - $\text{CH}_2\dot{\text{C}}\text{H} + \text{H}\dot{\text{N}}\text{O}$ (c) - $\text{CH}_2\dot{\text{C}}\text{H} + \text{H} + \text{NO}$ (d) Reichlen (1972) review | $k_a/k = 0.76 \pm 0.02$, $\lambda = 366\text{nm}$ $k_b/k = 0.24 \pm 0.04$, $\lambda = 366\text{nm}$ $(k_c + k_d)/k = 0.02$, $\lambda = 366\text{nm}$ $k = k_a + k_b + k_c + k_d$ |

REFERENCES

Reichlen, J., "Photochemical and Rate Data for Methyl Nitrite, Methoxy and Methylperoxy," Chemical Kinetics Data Survey V, Sixty-six Contributed Rate and Photochemical Data Evaluations on Ninety-four Reactions, NBSIR 73-206, D. Garvin, Eds. National Bureau of Standards, Washington, D.C. (1973) pages 43-48

R. F. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

No. Reaction/Reference Photochemical Data

600.00 $\text{CF}_3\text{Cl} + \text{hv} \rightarrow \text{products}$
NASA (1979) eval

| Absorption cross sections | | |
|---------------------------|------------------------------------|--|
| λ/nm | $10^{20} \text{ cm}^2/\text{mole}$ | |
| 184.6 | 0.36 | |
| 186.0 | 0.31 | |
| 187.8 | 0.23 | |
| 189.6 | 0.168 | |
| 191.4 | 0.126 | |
| 193.2 | 0.090 | |
| 195.1 | 0.064 | |
| 197.0 | 0.041 | |
| 199.0 | 0.026 | |
| 201.0 | 0.017 | |
| 203.0 | 0.012 | |

The cross section values given here are taken from the work of Chou et al (1978)

REFERENCES

- Chou, C. C., Milstein, E. J., Smith, W. S., Vera-Ruiz, E. V.,
Melina, M. J., and Bouland, F. S., "Stratospheric
Photodissociation of Several Saturated Perfluoro Chloro-
carbon Compounds in Current Technological Use (Fluoro-
carbons-12, -113, -114, and -115)," J. Phys. Chem. **82**,
1-7 (1978)
- NASA (1979). Recommendations of the NASA Panel for Data Evaluation,
published in NASA SP 1049 "The Stratosphere: Present and Future,"
E. D. Hudson and E. L. Reed, Editors, Dec. 1975 (report of the
June 1975 Harpers Ferry Workshop).
- E. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Photochemical Data

No. Reaction/Reference

61. hv $\text{CF}_2\text{Cl}_2 \rightarrow \text{hv} \rightarrow \text{products}$
 NASA (1979) eval

Absorption cross sections at 296K

| λ/nm | $10^{20} \sigma$ | λ/nm | $10^{20} \sigma$ |
|---------------------|------------------|---------------------|------------------|
| 186.0 | 106.0 | 205.1 | 2.55 |
| 187.8 | 85.4 | 207.3 | 1.50 |
| 188.6 | 64.6 | 209.4 | 0.85 |
| 191.4 | 48.7 | 211.6 | 0.51 |
| 193.2 | 35.3 | 213.9 | 0.25 |
| 195.1 | 24.5 | 216.2 | 0.17 |
| 197.0 | 16.6 | 218.6 | 0.095 |
| 198.0 | 10.8 | 221.0 | 0.05 |
| 201.8 | 6.87 | 223.5 | 0.05 |
| 203.0 | 4.36 | 226.0 | 0.05 |

$$\sigma_T = \sigma_{296} \exp[3.6 \times 10^{-4} (\lambda - 184.9)(T - 296)]$$

Where: σ_{296} : cross section at 296 K

λ : nm

T : temperature, Kelvin

CODATA (1979) eval

Detailed data sheet on photochemistry of CF_2Cl_2

The recommended values remain unchanged from NASA RP-1010. They are the mean of the values reported by Chou et al (1977), Robbins and Stolarski (1976) and Basm and Ledford (1978). The formula for temperature dependence is from Chou et al (1977). Vanlaethem-Neuree et al (1978) measured cross-sections as a function of temperature. At the lower temperatures their results are up to a factor of two smaller than those of Basm and Ledford (1978) and Chou et al (1977); they are, however, in agreement with the values at 214 nm reported by Rebhart and Austons (1975).

REFERENCES

- Basm, A. M., and Ledford, A. E. Jr., "Ultraviolet Photo-absorption Cross Sections of CF_2Cl_2 and CFCl_3 as a Function of Temperature," pages 282-284 in "12th Informal Conference on Photochemistry," M. J. Kurylo and W. Braun, Eds., Nat. Bur. Stand. (U.S.), Spec. Publ. 526 (1978)

- Chou, C. Co., Smith, W. So., Vera Ruiz, M., Moo, E., Crescentini, G.,
Molina, M. J., and Rowland, F. So., "The Temperature
Dependence of the Ultraviolet Absorption Cross Sections of
 CCl_2F_2 and CCl_3F , and their Stratospheric Significance,"
J. Phys. Chem. **81**, 286-290 (1977)
- CCDATA(1979). Recommendations of the CCData Task Group on Chemical
Kinetics. To be published in the Journal of Physical and Chemical
Reference Data.
- NASA RP-1010. "Chlorofluoromethanes and the Stratosphere"
R. D. Hudson, Editor, August 1977 This reference contains
the NASA (1977) rate constant recommendations.
- NASA (1979). Recommendations of the NASA Panel for Data Evaluation,
published in NASA RP 1049 "The Stratosphere: Present and Future,"
R. D. Hudson and E. L. Reed, Editors, Dec. 1979 (report of the
June 1979 Harpers Ferry Workshop).
- Hebert, R. E., and Ausloos, P. J., "Photodecomposition of
 CFCl_3 and CF_2Cl_2 ," *J. Photochem.* **3**, 415-434 (1975)
- Robbins, D. E., and Stolarski, R. So., "Comparison of Stratospheric
Ozone Destruction by Fluorocarbons 11, 12, 21 and 22," *Geophys.
Res. Lett.* **3**, 603-606 (1976)
- Vanlaethem-Meurice, M., Wisenberg, J., and Simon, P. Co.,
"Influence de la Température sur les Sections Efficaces
D'absorption des Chlorofluorométhanes dans l'ultraviolet,"
Bull. Acad. Roy. Belgique, Cl. Sci. **64**, 42-51 (1978)
- R. F. Hampson
June 1979

AD-AU91 631

NATIONAL BUREAU OF STANDARDS WASHINGTON DC CHEMICAL --ETC F/G 4/1
CHEMICAL KINETIC AND PHOTOCHEMICAL DATA SHEETS FOR ATMOSPHERIC --ETC
APR 80 R F HAMPSON DOT-FA79WAI-005

UNCLASSIFIED

FAA/EE-80-17

6 of 6

Fig. 3.

END
DATE
FILMED
12-80
DTIC

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

No. Reaction/Reference

Photochemical Data

62, hv $\text{CFCl}_3 \rightarrow \text{hv} \rightarrow \text{products}$
NASA (1979) eval

| λ/nm | Absorption cross sections | | | |
|---------------------|---------------------------|-------|-------|-------|
| | 213K | 232K | 252K | 298K |
| 186.0 | - | - | - | 243.0 |
| 187.8 | - | - | - | 217.0 |
| 189.6 | - | - | - | 186.0 |
| 191.4 | 161.0 | 161.0 | 164.0 | 159.0 |
| 193.2 | 137.0 | 137.0 | 141.0 | 133.0 |
| 195.1 | 110.0 | 110.0 | 114.0 | 111.0 |
| 197.0 | 88.5 | 88.5 | 91.3 | 90.3 |
| 199.0 | 69.1 | 69.1 | 72.1 | 73.0 |
| 201.0 | 53.1 | 54.3 | 56.6 | 57.3 |
| 203.0 | 40.2 | 41.1 | 43.0 | 45.2 |
| 205.1 | 28.6 | 30.0 | 31.7 | 33.3 |
| 207.3 | 19.8 | 21.1 | 22.6 | 23.9 |
| 209.4 | 13.3 | 14.2 | 15.2 | 16.8 |
| 211.6 | 8.5 | 9.1 | 9.9 | 11.5 |
| 213.9 | - | 5.7 | 6.4 | 7.6 |
| 216.2 | - | 3.4 | 3.9 | 5.0 |
| 218.6 | - | 2.0 | 2.3 | 3.1 |
| 221.0 | - | - | - | 2.0 |
| 223.5 | - | - | - | 1.2 |
| 226.0 | - | - | - | 0.8 |

CODATA (1979) eval

Detailed data sheet on photochemistry of CFCl_3

The recommended values remain unchanged from NASA RP-1010. The 298 K values are the mean of the values reported by Chou et al (1977), Robbins and Stolarski (1976) and Bass and Ledford (1978). The low temperature data of Chou et al (1977) are given here. The low temperature results of Bass and Ledford (1978) and of Vanlaethem-Neuree et al (1978) are in good agreement. The temperature effect at stratospherically important wavelengths is much smaller than for CF_2Cl_2 , but no such simple expression exists for CFCl_3 .

REFERENCES

- Beno, A. M., and Ledford, A. E. Jr., "Ultraviolet Photo-absorption Cross Sections of CF_2Cl_2 and CCl_3F as a Function of Temperature," pages 282-284 in "12th Internal Conference on Photochemistry," M. J. Kurylo and W. Brown, Eds., Nat. Bur. Stand. (U.S.), Spec. Publ. 536 (1979)
- Chou, C. C., Smith, R. S., Vera Ruiz, M., Moo, K., Crescentini, G., Mellina, M. J., and Rowland, F. S., "The Temperature Dependences of the Ultraviolet Absorption Cross Sections of CCl_2F_2 and CCl_3F , and their Stratospheric Significance," *J. Phys. Chem.*, **81**, 286-290 (1977)
- COMDATA(1979), Recommendations of the COMDATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.
- NASA RP-1010, "Chlorofluoromethanes and the Stratosphere" R. S. Hudson, Editor, August 1977 This reference contains the NASA (1977) rate constant recommendations.
- NASA (1979), Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," R. S. Hudson and E. L. Reed, Editors, Dec. 1975 (report of the June 1979 Harpers Ferry Workshop).
- Robbins, R. E., and Stolarski, R. S., "Comparison of Stratospheric Ozone Destruction by Fluorocarbons 11, 12, 21 and 22," *Geophys. Res. Lett.*, **3**, 603-606 (1976)
- Vanlaethem-Mouries, M., Wisniberg, J., and Simon, P. C., "Influence de la Température sur les Sections Efficaces d'absorption des Chlorofluorométhanes dans l'ultraviolet," *Bull. Acad. Roy. Belgique, Cl. Sci.*, **54**, 42-51 (1978)
- R. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

No Reaction/Reference Photochemical Data

63. hv CCl₄ + hv - products

CODATA (1976) eval

Absorption cross sections

| λ/nm | 10^{20} s^{-1} | λ/nm | 10^{20} s^{-1} |
|---------------------|--------------------------|---------------------|--------------------------|
| 176 | 1007 | 208 | 52.0 |
| 180 | 772 | 212 | 39.7 |
| 184 | 450 | 216 | 27.2 |
| 188 | 218 | 220 | 17.0 |
| 192 | 98.9 | 224 | 9.6 |
| 196 | 68.2 | 228 | 5.5 |
| 200 | 64.8 | 232 | 3.0 |
| 204 | 60.4 | 236 | 1.5 |

REFERENCES

CODATA(1976). Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.

B. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Photochemical Data

No. Reaction/Reference

68.40 $\text{CH}_3\text{CCl}_3 \xrightarrow{h\nu} \text{products}$
 This survey

Absorption cross sections

| $\lambda/\text{m}\mu$ | (a) | (b) |
|-----------------------|---|-------|
| | $\times 10^{20} \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ | |
| 186.0 | 325.0 | 305.0 |
| 187.0 | 284.0 | 225.0 |
| 189.0 | 246.0 | 200.0 |
| 191.4 | 212.0 | 175.0 |
| 192.2 | 195.0 | 152.0 |
| 195.1 | 168.0 | 129.0 |
| 197.0 | 148.0 | 108.0 |
| 199.0 | 128.0 | 88.0 |
| 201.0 | 111.0 | 72.5 |
| 203.0 | 95.4 | 59.0 |
| 208.1 | 80.5 | 46.0 |
| 209.3 | 63.9 | 35.5 |
| 209.4 | 51.1 | 25.8 |
| 211.6 | 35.4 | 19.0 |
| 212.9 | 28.1 | 12.8 |
| 216.2 | 15.6 | 8.4 |
| 218.6 | 12.5 | 5.4 |
| 221.0 | 8.3 | 3.6 |
| 222.5 | 5.1 | 2.3 |
| 226.0 | 2.9 | 1.5 |

(a) NASA (1979)
 (b) Vanlaethem-Meuree et al (1979)

No recommendation is given here. Two sets of cross section data are tabulated. The values in column(a) are the NASA (1979) values which are taken from P. A. Hewland (private communication, 1976). The values in column(b) are taken from the very recent study by Vanlaethem-Meuree et al (1979). These latter values are significantly lower than the NASA (1979) values and yield a calculated photodissociation rate which is nearly a factor of two smaller.

REFERENCES

- NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," R. R. Fiedson and E. J. Reed, Editors, Dec. 1975 (report of the June 1975 Harpers Ferry Workshop).
- Vanlaethem-Mourde, M., Wisenbert, J., and Simon, P. Co., "Ultraviolet Absorption Spectrum of Methylchloroform in the Vapor Phase," Geophys. Res. Lett., 6, 451-454 (1979)
- R. R. Fiedson
June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Photochemical Data

No. Reaction/Reference

CF₂O + hv → products
 CFCl₃ + hv → products
 CCl₂O + hv → products
 NBSA (1979) eval

Absorption cross sections

| λ/nm | $\sigma_{\text{CCl}_2\text{O}}$ | σ_{CFCl_3} | $\sigma_{\text{CF}_2\text{O}}$ |
|---------------------|---------------------------------|--------------------------|--------------------------------|
| 184.9 | 204.0 | | 4.7 |
| 186.0 | 189.0 | 15.6 | 5.5 |
| 187.8 | 137.0 | 14.0 | 5.2 |
| 189.6 | 117.0 | 13.4 | 4.5 |
| 191.4 | 93.7 | 12.9 | 4.0 |
| 193.2 | 66.7 | 12.7 | 3.3 |
| 195.1 | 52.5 | 12.5 | 2.8 |
| 197.0 | 41.0 | 12.4 | 2.3 |
| 199.0 | 31.8 | 12.3 | 1.9 |
| 201.0 | 25.0 | 12.0 | 1.4 |
| 203.0 | 20.4 | 11.7 | 1.1 |
| 205.1 | 16.5 | 11.2 | 0.86 |
| 207.3 | 15.1 | 10.5 | 0.65 |
| 209.4 | 13.4 | 9.7 | 0.48 |
| 211.6 | 12.2 | 9.0 | 0.36 |
| 213.9 | 11.7 | 7.9 | 0.26 |
| 216.2 | 11.6 | 6.5 | 0.21 |
| 218.6 | 11.5 | 5.8 | 0.15 |
| 221.0 | 12.2 | 4.8 | 0.12 |
| 223.5 | 12.8 | 4.0 | 0.10 |
| 226.0 | 13.2 | 3.1 | 0.08 |

COBATA (1979)

Detailed data sheets on photochemistry of these species

The absorption cross sections of CCl₂O (phosgene), CFCl₃, and CF₂O are taken from the work of Chen et al (1977a). The spectrum of CF₂O shows considerable structure. The values listed here are averages over each 50-wave number interval. Preliminary photochemical studies (Chen et al 1977a) indicate unit quantum yield for photodissociation at 184 nm. The spectrum of CFCl₃ shows less structure, and the CCl₂O spectrum is a continuum; its photodissociation quantum yield is unity (Calvert and Pitts, 1967).

REFERENCES

- Colvert, J. G., and Pitts, J. N., Photochemistry, John Wiley & Sons, Inc., New York, No. 220-231 (1967)
- Chen, C. C., Crescentini, G., Vera-Ruiz, M., Smith, W. S., and Newland, F. S., "Stratospheric Photochemistry of CF_2O , OCIO and Cl_2O ," 173rd American Chemical Society National Meeting, New Orleans (1977a)
- COMATA (1979), Recommendations of the COMATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.
- NASA (1979), Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1099 "The Stratosphere: Present and Future," B. B. Hudson and H. I. Reed, Editors, Dec. 1975 (report of the June 1974 Harpers Ferry Workshop).
- B. B. Hudson
June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS
Photochemical Data

No. Reaction/Reference

68.40 $\text{CClF}_2\text{CF}_3 + \text{h}\nu \rightarrow \text{products}$
 $\text{CClF}_2\text{CClF}_2 + \text{h}\nu \rightarrow \text{products}$
 $\text{CClF}_2\text{CCl}_2\text{F} + \text{h}\nu \rightarrow \text{products}$
 NBSA (1979) eval

| λ_{max} | Absorption cross sections | | |
|------------------------|----------------------------|------------------------------|-------------------------------------|
| | CClF_2CF_3 | $\text{CClF}_2\text{CClF}_2$ | $\text{CClF}_2\text{CCl}_2\text{F}$ |
| 166.0 | 0.61 | 10.0 | 105.0 |
| 167.8 | 0.49 | 7.91 | 85.0 |
| 169.6 | 0.36 | 5.97 | 68.9 |
| 171.4 | 0.27 | 4.44 | 53.8 |
| 173.2 | 0.20 | 3.13 | 41.0 |
| 175.1 | 0.14 | 2.52 | 30.0 |
| 177.0 | 0.093 | 1.54 | 21.3 |
| 179.0 | 0.066 | 1.00 | 14.9 |
| 201.0 | - | 0.67 | 10.4 |
| 203.0 | - | 0.44 | 7.0 |
| 205.1 | - | 0.30 | 4.7 |
| 207.3 | - | 0.18 | 3.2 |
| 209.4 | - | 0.11 | 2.05 |
| 211.6 | - | 0.063 | 1.26 |
| 213.9 | - | 0.043 | 0.78 |
| 216.2 | - | - | 0.47 |
| 218.6 | - | - | 0.29 |

The cross section values given here for CClF_2CF_3 (fluorocarbon 115) and for $\text{CClF}_2\text{CClF}_2$ (fluorocarbon 114) are the mean of the results reported by Chow et al (1978) and by D. E. Robbina, private communication (1976). The values given here for $\text{CClF}_2\text{CCl}_2\text{F}$ (fluorocarbon 113) are those reported by Chow et al (1978)

REFERENCES

- Chou, C. C., Milstein, B. J., Smith, W. S., Vera-Ruiz, E. V.,
 Molina, M. J., and Rowland, F. S., "Stratospheric
 Photodissociation of Several Saturated Perhalo Chlorofluoro-
 carbon Compounds in Current Technological Use (Fluoro-
 carbons-12, -113, -114, and -115)," J. Phys. Chem. **82**,
 1-7 (1978)

NASA (1979). Recommendations of the NASA Panel for Data Evaluation,
published in NASA EP 1049 "The Stratosphere: Present and Future."
R. B. Hudson and E. L. Reed, Editors. Dec. 1975 (report of the
June 1975 Barbers Ferry Workshop).

R. P. Hampson
June 1979

END

DATE
FILMED

12-80

DTIC